A Speleothem-Based High Resolution Reconstruction of Climate in Southeastern Brazil Over the Past 4,100 Years

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A SPELEOTHEM-BASED HIGH RESOLUTION RECONSTRUCTION OF CLIMATE IN SOUTHEASTERN BRAZIL OVER THE PAST 4,100 YEARS

A Thesis Presented

by

BRANDON LEE TAYLOR

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirements for the degree of

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Department of Geosciences
A SPELEOTHEM-BASED HIGH RESOLUTION RECONSTRUCTION OF CLIMATE IN SOUTHEASTERN BRAZIL OVER THE PAST 4,100 YEARS

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ABSTRACT

A SPELEOTHEM-BASED HIGH RESOLUTION RECONSTRUCTION OF
CLIMATE IN SOUTHEASTERN BRAZIL OVER THE PAST 4,100 YEARS

FEBRUARY 2010

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Isotopic investigations of speleothem CR1 from Cristal Cave in southeastern Brazil have established a high-resolution record of climate change extending 4,100 years prior to sample collection in 2007. A total of 14 subsamples were collected from CR1 for U/Th age determination. ICP-MS analysis yielded very precise ages with analytical errors (2σ) averaging ± 13 years. An initial growth rate of .062 mm y⁻¹ for the first 2860 years is followed by a rate of .08 mm y⁻¹ for the remaining growth period allowing for sampling of δ¹⁸O at sub-decadal resolution. Stable isotope analyses show a large range of δ¹⁸O values between -7.5 ‰ to -4 ‰. The data show a trend of steadily decreasing values over the past 4,000 y BP. The exception to this trend is the last 150 years BP when some of the least negative and most variable values for the record are observed.

Variations in speleothem δ¹⁸O in southern Brazil have been shown to reflect changes in rainfall δ¹⁸O, which in turn indicate changes in rainfall source or rainfall amount (Cruz et al., 2006). In Southeastern Brazil, δ¹⁸O is controlled mainly by moisture source location, in particular South American monsoonal versus extratropical sources
The relative contribution of monsoonal and extratropical moisture help to define the $\delta^{18}O$ of regional precipitation via the mean location and southward extent of Hadley cell convective activity associated with the South American summer monsoon (Cruz et al., 2005). For example, decreases in precipitation $\delta^{18}O$ are often interpreted as a decreased contribution of winter versus summer precipitation (Cruz et al., 2005). Assuming that the modern (observed) relationship between the seasonality and moisture source location effect occurring in southeastern Brazil have functioned for the past ~ 4,100 years, trends of more negative values towards modern day are likely due to increased summer precipitation and/or an overall increase in total yearly precipitation. The more enriched values of the past 100 years suggest a recent decrease in summer and/or total rainfall.
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CHAPTER 1
INTRODUCTION

Extending climate records beyond the period of instrumental observation has long been the goal of paleoclimate researchers worldwide. Instrumental records of climate often extend for only a few decades or centuries and are spatially limited compared to the relatively broad distribution of paleoclimate proxies. Utilizing proxies to reconstruct past climates makes it possible to greatly increase the spatial and temporal resolution of data sets which allow for a more complete conceptual understanding of local and global scale climate dynamics.

In order to fully understand the relationship between climate and the mechanisms responsible for its variability it is necessary to reconstruct a record with a useful temporal resolution and length. Depending on the climate systems of interest, records ranging in duration from decades to hundreds of thousands of years with temporal resolutions recording annual to millennial change may hold equal value. Meaningful climate data has traditionally been coaxed from archives such as ice cores, tree rings and lake sediments, producing records extending several hundred thousand years. These archives have largely been effective in extending knowledge of natural and anthropogenically induced climate variability but are often spatially limited. For example, the environment conducive to the formation and the long term viability of glaciers makes ice core data available for only a small area of the earth. The same is true for both tree rings and lake sediments. Although they are relatively common materials, few tree rings and lake sediments are linked to a setting that allows for meaningful paleoclimate reconstruction.
Speleothems, the general term for cave formations like stalactites and stalagmites enjoy a fairly broad global distribution and can provide a climate record extending several tens of thousand years into the past with temporal resolutions as fine as annual. The information offered by speleothems is varied and includes factors related to climate such as local precipitation amount, seasonal timing of precipitation, geographic source of precipitation, local aridity and local vegetation cover (Fleitmann et al., 2008).

Although a variety of information can be gleaned from speleothems, the principle data set generated for this investigation give indications of precipitation amount and moisture source location for resultant precipitation. Both of these attributes are recorded through variations in stable oxygen isotopic composition of speleothem calcite. For this investigation, a stalagmite (sample CR1) collected from Cristal Cave, Iporanga municipality, Brazil will be examined (Figure 1). Sample CR1 was active when collected in 2007 and offers a precisely dated record of climatic change over southeastern Brazil for the last ~ 4.1 kyr.
Figure 1 – Cristal Cave (24° 34'41" S; 48° 35'00" W).
CHAPTER 2
MODERN CLIMATE

2.1 Modern Brazilian Climate and South American Circulation Features

The modern climate of southeastern Brazil is best characterized as subtropical, with a relatively even distribution of precipitation and temperature throughout the year. The typical range of yearly precipitation is between 1250 mm and 2000 mm and temperatures range between 17-24ºC (Behling, 2002). Precipitation is not distributed with perfect regularity however, as a slightly greater percent of total year precipitation falls during October through March. The Köppen Climate classification of southeastern Brazil is Cf (temperate subtropical, humid) and much of the vegetation in the region is comprised of tropical-like deciduous rainforests (Sparovek, 2007; Van Lier, Neto, 2007). During the austral summer the prevailing wind is from the northwest and moisture is sourced from the Amazon Basin. At the onset of austral winter, prevailing winds bring moisture from the nearby subtropical Atlantic Ocean for the duration of the season.

The seasonal migration of the Intertropical Convergence Zone (ITCZ) plays a large role in regulating the climate of South America. The seasonal cycle and distribution of tropical/subtropical rainfall over the central mass of the continent is largely the result of the contrast between the relatively low thermal inertia of land and the high thermal inertia of the ocean (Garreaud et al., in press). As such, migration of the ITCZ can be categorized into phases of distinct behavior and linked to changes in seasonality. During the austral winter, the maximum continental rainfall is typically located north of the
equator and is nearly concordant with the oceanic ITCZ. When the ITCZ is at its most northward position, the majority of the continental interior remains relatively dry. As the seasons progress into austral summer, maximum precipitation occurs within the southern most half of the Amazon Basin into Northern Argentina. During the austral fall the ITCZ and the location of maximum precipitation moves gradually northward, eventually reaching the northern extent of South America. The movement of the ITCZ to its southernmost position over the Amazon Basin results in a unique situation whereby large amounts of moisture are available for intense convection associated with the southernmost position of the ITCZ. This intense convection results in much rainfall in southeastern Brazil and is one of the features that help to define the South American Monsoon System (SAMS).

The SAMS is a critical circulation feature for southeastern Brazil due to the fact that it is responsible for modulating the summer time rainfall that accounts for the majority of precipitation falling over this region of South America. Although it is active only during the austral summer, the SAMS affects the yearly climate of tropical and subtropical Brazil due to the fact that the amount and intensity of summertime rainfall is so dependent upon it. The effects of the timing and strength of the SAMS also have an influence that extends across much of the continent. Although the SAMS is not a “classic” monsoon in the sense that there is no seasonal reversal of wind patterns associated with its onset, precipitation linked to the SAMS is responsible for a large portion of the annual precipitation in southeastern Brazil. The SAMS and the Indian Ocean Monsoon (IOM) are similar in that both features develop over a land mass located near the equator and are partially influenced by high mountains which help to block low
level circulation. Not only are some regional circulation features common between the two, but also the onset of the SAMS and IOM season are defined by the onset of sudden, intense summertime precipitation. As one would expect with circulation features that develop in different hemispheres at different times of the year, the SAMS is unique. These features are most prominent during the austral summer (DJF) and include a large-scale land ocean temperature gradient and development of low pressure over the continental interior (Chaco low) in conjunction with high pressure (Bolivian high), which exhibits anticyclonic circulation at higher altitudes (Vuille and Werner 2005). Vuille and Werner (2005) choose to define the strength of the SAMS by using the degree of convective activity over the center of summer convection, a convention that will be maintained throughout this report.

Once the SAMS is established during the austral summer, it is responsible for nearly 50% of the annual precipitation falling in tropical and subtropical South America (Vuille and Werner 2005). As discussed by Vuille and Werner (2005), the SAMS is notably different from the maritime ITCZ, which is often incorrectly used to explain the entirety of seasonal movement of precipitation over South America. Most of the moisture for wintertime rainfall is provided by mid-latitude cyclones from the subtropical Atlantic (Vera et al., 2004). The Pacific Ocean may not play as large of a role in modulating the intensity of the SAMS as the Atlantic Ocean, primarily because the Andes effectively block any low level influence of the Pacific Ocean on South America. However, it is still important to note the contrast between cold (~22.5°C) Pacific SST immediately off the coast of Peru and Ecuador and the relatively warm SST (~27°C) in the tropical Atlantic. Even with the blocking influence of the Andes, warm Pacific SSTs
may influence ENSO activity, which may in turn indirectly influence SAMS strength (Vuille and Werner 2006).

Although the SAMS accounts for the majority of summertime precipitation falling over southeastern Brazil, it is also important to address the source of wintertime precipitation. The fact that there is a distinct geographic separation between the two sources allows for the reconstruction of the seasonal timing of precipitation, a scenario that will be addressed in the Discussion section of this report. While the majority of precipitation falling over southeastern Brazil during the austral summer is derived from intense convection over the Amazon Basin, wintertime precipitation is more locally sourced. In fact, most wintertime precipitation is derived from surface waters immediately off the coast, in the southwestern Atlantic. Convection is relatively moderate and the resultant moisture is transported over the region by local trade winds. Perhaps most importantly for this study, modern, locally derived wintertime precipitation has an average $\delta^{18}O$ of -3‰ while summer time precipitation has $\delta^{18}O$ values of -7‰ (Cruz et al., 2005).

**2.2 Worldwide and Continental Scale Distribution of Stable Isotopes in Precipitation**

The distribution of stable isotopes in precipitation is governed by several factors including moisture source location, local meteoric conditions, worldwide climatic conditions, location of precipitation, and continental topography. Isolation of the various factors contributing to stable isotope distribution can be difficult, however the following section will address factors that directly influence the isotopic makeup of precipitation in South America.
Figure 2 - Worldwide distribution of stable isotopes ($\delta^{18}O$) in meteoric precipitation. Note that many values have been interpolated based on the measured isotopic values of precipitation from GNIP collection sites (IAEA, 2001).

Global scale meteoric precipitation displays a fairly large range, as shown in Figure 2. In the case of the weighted annual average, a per mille ($‰$) range of approximately 30 is sufficient to describe most precipitation on Earth, although most interpolated $\delta^{18}O$ values are between $–10$ to $–14$ $‰$. Several patterns may be noted when looking at the worldwide distribution of isotopes. Perhaps foremost among them is that precipitation becomes increasingly depleted as it falls at higher latitudes and further away from its moisture source near the equator. Of course, there are areas where this pattern does not hold true, most notably near the Andes Mountains of South America and the
Tibetan Plateau of Central Asia. Discrepancies in these locations are caused largely by orographically induced rainout of heavy isotopes ($^{18}$O) resulting in subsequent depletion of the resultant precipitation. A similar rainout effect is observed near continental interiors. As precipitation falls nearer to the middle of a continent and thus further away from its source location, it becomes more depleted relative to the heavy isotope. This results in the familiar global meteoric water line (Figure 3).

![Global Precipitation](image)

Figure 3 - Global meteoric water line (Clark and Fritz 1997).

The meteoric water line used to describe the isotopic evolution of precipitation moving towards a continental interior is similar to that which describes the evolution of precipitation moving away from its source location (i.e. precipitation moving poleward from the tropics). Due to the common mechanisms that govern the isotopic composition
of meteoric precipitation the following explanation is applicable to precipitation on both a continental and global scale.

Mass differences and the resultant discrepancies in vapor pressures of H$_2^{16}$O and H$_2^{18}$O result in distinct $\delta^{18}$O values of liquid water and the resultant water vapor. For example, water vapor forming from seawater; because the stable isotopic standard for water is SMOW (Standard Mean Ocean Water) it can be expected that seawater will have a $\delta^{18}$O value of approximately zero. Since the phase transition between liquid and vapor effectively discriminates against $^{18}$O due to its higher vapor pressure, the resultant vapor will be enriched in $^{16}$O and depleted in $^{18}$O. As the body of water vapor moves away from its source, condensation and precipitation will continue to occur. However since the body of vapor is no longer near its source there will be no new supply of $^{18}$O and the resulting precipitation will become increasingly depleted in $^{18}$O. The cycle of continual rain out of the heavy isotope coupled with a lack of additional $^{18}$O leads to continual depletion (more negative $\delta^{18}$O values) of the resultant precipitation. This relationship results in the meteoric water line as shown in Figure 3. It is important to note that in addition to fractionation that takes place during the transition between liquid and vapor there is also fractionation that occurs when vapor condenses to liquid. Instead of the heavy isotope being discriminated against and left in the liquid, condensate formed from vapor preferentially incorporates the heavy isotope. Thus precipitation derived from vapor is isotopically heavier than the vapor itself.

Deviations from this line can often be explained by the introduction of outside moisture via large lakes, rivers or exceptionally moist vegetation. In some cases, evapotranspiration effectively serves to dampen the expected results of the continental
isotope effect by negating much of the fractionation that would normally take place in the transition of groundwater to water vapor. Fractionation does take place during evapotranspiration, however the net fractionation of water vapor entering the atmosphere is effectively zero (Worden et al., 2007).

Not only do continental isotope effects have an influence on the stable isotopic composition of precipitation, the well documented “amount effect” can also play a vital role in determining the makeup of meteoric precipitation. This phenomenon results in the volume of precipitation and $\delta^{18}O$ of resultant precipitation having an inverse relationship. The processes that result in this outcome are not fully understood, though there are several possibilities as to the cause of this phenomenon. When vapor condenses to a liquid the heavy isotope is favored resulting in precipitation that is isotopically enriched compared to subsequent precipitation. As such, relatively small amounts of precipitation will result in relatively high (less negative) $\delta^{18}O$ values. When large amounts of precipitation fall, there is more opportunity for $^{16}O$ to condense from vapor, thereby resulting in precipitation with relatively lower (more negative) $\delta^{18}O$ values.

For investigations in southeastern Brazil the topography, local atmospheric circulation and vegetation cover help to create a unique situation in regards to stable isotopes in precipitation. In the case of precipitation falling over much of southeastern Brazil, isotopic composition is not governed entirely by the “amount effect.” Instead, the $\delta^{18}O$ of precipitation may indicate the moisture source, precipitation amount or the seasonal balance of precipitation (Cruz et al., 2006). The source of moisture is often divided into either monsoonal or extratropical. Whether or not precipitation is sourced from either of these two reservoirs is determined primarily by the location of local
Hadley Cell convective activity and the southward extent of the South Atlantic Convergence Zone (Figure 4) (Cruz et al., 2005). The relationship is such that when the SAMS is in an intensified state, water vapour is moved toward the SACZ by a low level jet and the resultant precipitation is depleted in $\delta^{18}$O in regard to its original source (Cruz et al., 2005). This relationship also links enhanced SACZ activity to increased precipitation over southeastern Brazil due to increased moisture transport along the low level jet (Mechoso, 2000; Leibman et al., 2004). Thus, the $\delta^{18}$O of precipitation in southeastern Brazil is indicative of the relative proportion of summer versus winter time rainfall and/or overall increasing or decreasing total precipitation amount.

Figure 4 - Mean monthly precipitation averaged for 1979 – 2004 over South America helps to identify the development and location of the SACZ. During DJF (left panel) SACZ is well developed and is the primary source of precipitation for southeastern Brazil (Cristal Cave shown by number 1), while during JAS precipitation is more locally sourced (right panel) (Figure after Cruz, et al., 2005).
CHAPTER 3
LITERATURE REVIEW

3.1 Introduction

Paleoclimate reconstruction through the use of speleothems often provides a valuable record of past climate change that can span millennia with extremely accurate and precise chronologies. However, it is important to keep in mind that relying on a single proxy to establish spatially and temporally broad hypotheses is undesirable and may lead to overly broad assumptions. It is possible that individual proxies do not provide a complete or entirely accurate account of climate change. For this reason it is important to examine multiple proxies whenever possible. Fortunately, research has been focused on South America such that archives are readily available for comparison, including other speleothems, lake and anoxic basin sedimentary geochemical and pollen records, as well as output from regional circulation models.

3.2 Speleothems

It was not until the mid to late 1960’s that it was recognized that geochemical evidence for climate change was archived in speleothems. Although not the first to publish on this topic, Hendy and Wilson (1968) were among the first to recognize the fundamental processes involved in stable isotope studies of speleothems and were also among the first to apply these new concepts to field investigations. Hendy and Wilson (1968) argued that in order to best understand Pleistocene climatic variability it is desirable to examine proxy records that are geographically distant from ice sheets and their proximal effects. Until the mid 1960’s, many paleoclimate proxies were derived from terrestrial records which would have been geographically close to ice margins of the
Last Glacial Maximum. More importantly, it was thought that temperature fluctuations close to ice sheets would not be representative of those on a larger scale. Speleothems offered the opportunity to examine paleoclimate records archived over a temporally and geographically widespread area.

By the mid 1960’s oxygen isotopes were already recognized as a tool for examining calcareous ocean sediments. However, Hendy and Wilson (1968) realized that slow deep sea sediment deposition rates made the likelihood of obtaining high resolution records from those materials rare. Yet even in these early investigations, Hendy and Wilson (1968) were able to obtain a preliminary speleothem δ¹⁸O record with a point resolution of 1 kyr, about three times as great as then-current oceanic sediment core records. This work by Hendy and Wilson (1968) also pioneered the now frequently used “Hendy Test”, whereby δ¹⁸O and δ¹³C are measured along a single growth layer in order to determine whether or not the stable isotopic composition of calcite has been influenced by in-cave kinetic fractionation effects.

Later work by Hendy (1971) relied on geochemical modeling to show how various isotope effects accompany different modes of speleothem calcite deposition. Hendy (1971) determined that records of past climate change are best archived in δ¹⁸O values, a measurement that relies on the ratio of isotopes, not absolute isotope abundance. It was also posited that it is not possible to directly determine paleotemperatures via δ¹⁸O values, as is the case with benthic foraminifera. Instead, many variables are involved in determining the δ¹⁸O of speleothem calcite and analyses and interpretation should be considered separately from foraminiferal studies.
This subsequent work by Hendy (1971) argued a very important point for speleothem paleoclimatologists; given proper conditions, $\delta^{18}O$ of speleothem calcite is directly attributable to $\delta^{18}O$ of meteoric water (and thereby climatic and meteorologic controls), not local in-cave effects. Most critical to his argument, Hendy (1971) showed that the rate of CO$_2$ degassing must be slow in order for isotopic equilibrium to be maintained. If degassing occurs too quickly, the subsequent loss of CO$_2$ will prevent isotopic equilibrium between CO$_2$ and HCO$_3^-$ from being achieved. Hendy (1971) concludes that if approximately half of the bicarbonate solution “converts” to CO$_2$ and CaCO$_3$ in less than $\sim 2 \times 10^3$ seconds, the oxygen isotopic composition of the freshly precipitated calcite will be in isotopic equilibrium with O$_2$ in the drip water. It should be noted that this rather straightforward interpretation applies only to oxygen isotopes and that carbon isotopes (to be discussed later) are governed by slightly different processes.

It is important to note that this early work by Hendy only deals with isotopic distribution within cave systems and does not address isotope distribution and temperature dependant isotope composition on a global scale. However, stable isotopic composition of meteoric precipitation and atmospheric transport mechanisms governing the distribution of stable isotopes is of vital importance to the understanding of stable isotope based speleothem climate studies.

### 3.3 Southeastern Brazilian Speleothems

Widely recognized paleoclimate archives such as the laminated sediments of the anoxic Cariaco Basin offer the opportunity to extend records of climatic variability over northern South America for the last ~ 90 kyr at decadal resolution (Deplazes et al., 2009). It is tempting to use such thoroughly examined archives in order to better understand
variability observed in speleothems from southeastern Brazil. However, examining Cariaco Basin sediments in reference to CR1 stable isotope values is not a direct measure of the coherence between the two proxies and in this scenario relies on looking for anti-correlations related to movement of the ITCZ. Ideally, CR1 could be compared to nearby speleothem records that span a similar time interval at an equally high resolution. Unfortunately, such speleothem records are currently rare. One thoroughly examined paleoclimate archive is offered by stalagmite Bt2 (Cruz et al. 2005), a 116 kyr speleothem record from Botuverá Cave in southeastern Brazil. Although the temporal resolution of Bt2 is coarser than CR1, the location and precise dating of Bt2 offer the opportunity to compare the last ~ 4.1 kyr of Bt2 with CR1. Most importantly, Bt2 likely responds to the same climatic signals that govern the $\delta^{18}O$ of CR1. The $\delta^{18}O$ of Bt2 is not dominated by the “amount effect” as is the case with most speleothems in the tropics and sub-tropics; instead $\delta^{18}O$ varies according to precipitation moisture source location (Cruz et al., 2005). Through the analysis of modern precipitation, Cruz et al. (2005) determined that $\delta^{18}O$ values and trends are likely indicative of the relative proportion of winter versus summer precipitation. The characteristic annual distribution of winter versus summer precipitation is primarily controlled by the mean location and southernmost extent of SAMS convective activity as well as the southern boundary of the Hadley cell (Cruz et al., 2005). However, the “amount effect” still plays a role in determining $\delta^{18}O$ of speleothems from southeastern Brazil, as is the case with nearly all speleothems from the tropics and subtropics. It may be possible that by comparing CR1, Bt2 and modern instrumental precipitation data an overprinted amount effect signal can be delineated from the overall $\delta^{18}O$ value.
Stalagmite Bt2 is useful because a variety of techniques have been used to extract paleoclimate data from it. As previously noted, $\delta^{18}O$ of speleothem calcite from stalagmites collected in southeastern Brazil is largely determined by moisture source location, not the amount or intensity of regional precipitation. Bt2 offers a record that extends over several precessional cycles and Cruz et al. (2005) is able to link changes in Bt2 $\delta^{18}O$ with millennial scale insolation driven changes in atmospheric circulation, mainly the intensity and southward extent of the South American Southern Monsoon (SAMS) and the mean location of the South Atlantic Convergence Zone (SACZ). In general it is noted that Bt2 $\delta^{18}O$ values became increasingly more negative during the course of the Holocene leading towards modern day, which is in general agreement with palynological records indicating the expansion of the Atlantic rainforests near the coast of southern Brazil (Cruz et al., 2005).

In subsequent work Cruz et al. (2006) again examined Bt2, but expanded on concepts presented in earlier work by constructing a record of soil processes and atmospheric circulation using stable carbon isotopes from speleothem calcite. As previously mentioned, $\delta^{13}C$ analysis of speleothem calcite is more complicated than that of $\delta^{18}O$ as carbon isotopes are governed by several additional processes which do not affect oxygen isotopes. Cruz et al. (2006) address these issues in order to effectively reconstruct changes in large-scale atmospheric circulation and the influence these changes have on the temperature-driven controls of biologic activity and soil CO$_2$ productivity.
Stable carbon isotope values can be interpreted in a variety of ways, however Cruz et al. (2006) posited that $\delta^{13}C$ of speleothem calcite in southeastern Brazil is primarily influenced by the biogenic supply of CO$_2$ from soil overlying the cave. In turn, the $\delta^{13}C$ of CO$_2$ produced in overlying soil is largely dependant upon temperature and rainfall amount (Cruz et al., 2006). Since the mechanisms leading to variation of $\delta^{13}C$ in speleothem calcite are mentioned in Chapter 8 only the primary conclusions of Cruz et al. (2006) will be addressed here.

Although many mechanisms are responsible for the observed variability of $\delta^{13}C$ in speleothem calcite, Cruz et al. (2006) determined that variability within Bt2 is primarily the result of fluctuations in local temperature and precipitation. Cruz et al. (2006) ruled out other known influences such as changes in vegetation type (C3 versus C4), changes in the bedrock dead carbon fraction and enhanced kinetic fractionation effects within the cave in order to assert that moisture availability and local temperature were responsible for $\delta^{13}C$ variability. However, it should be noted that this is only true for several time intervals, including the most recent ~7.5 kyr BP (which is applicable to CR1). One of the most telling lines of evidence is that $\delta^{13}C$ variability in Bt2 is due to changes in rainfall and temperature is that Behling and Negrelle (2001) used palynological evidence to determine that rainforest dominated the lowlands of southeastern Brazil since ~7.5 kyr marking the late Holocene as a period of increased moisture availability. In accordance with local climatology, it was found that after ~18 kyr BP, negative and positive excursions of $\delta^{13}C$ in Bt2 correspond to enhanced summer
monsoon activity and more intense extratropical circulation over southeastern Brazil (Cruz et al., 2006).

The final technique applied to Bt2 was analysis of trace element (Sr and Mg) ratios to help determine relative regional aridity (Cruz et al., 2007). This process required scanning electron microprobe analysis in order to determine Mg/Ca and Sr/Ca ratios of the speleothem carbonate. These ratios are useful because they offer a relative measure of prior calcite precipitation, which in turn is used as a measure of local aridity. The interpretation that trace element ratios are controlled by the rate of meteoric water infiltration has been confirmed by modern hydrochemistry studies (Fairchild et al., 2000, Tooth and Fairchald 2003). Although modern studies have confirmed that the infiltration rate of meteoric precipitation has primary control on trace element ratios, it is possible that other processes are responsible for influencing these ratios.

When looking specifically to Mg/Ca and Sr/Ca, there are three factors, which influence the relative concentration of these trace elements within speleothem calcite. Foremost is the composition of the drip water, which is often invoked in this type of study and is the factor that is thought to govern trace element ratios in Bt2 (Cruz et al., 2007). It is also possible that in-cave temperature fluctuations have an effect on trace element ratios, but the typical range of temperature variability observed in caves is generally not great enough over the active life of a speleothem to cause significant deviation of trace element ratios. In addition to changes in trace element ratios due to drip water chemistry and in-cave temperature fluctuations, growth rate may play a role in regulating Mg/Ca and Sr/Ca. Although the influence of increased growth rates have been shown to play a role in the trace element composition of stalagmites in laboratory studies.
(Huang and Fairchild 2001) the growth rates cited are exceedingly fast for the vast majority of speleothems in nature.

Cruz et al. (2007) was able to delineate complicating factors relating to the trace element ratios of Bt2 and determined that Mg/Ca and Sr/Ca varied in accordance with southern hemisphere summer insolation. Generally dryer conditions prevailing during phases of low summer insolation coincide with decreased activity of the South American summer monsoon and vice versa. In regards to the time period archived by both Bt2 and CR1, trace element ratios show a general trend towards increasingly wetter conditions during the late Holocene.

Botuverá Cave is favorably situated in the mind of speleothem based paleoclimatologists because it offers an abundance of naturally broken speleothems, mitigating ethical questions associated with the collection of active stalagmites. Although this method increases the possibility that the proxy record will not extend to modern day, it does facilitate the construction of a temporally long “composite’ record. Recent work by Wang et al. (2007) and Wang et al. (2006) has confirmed many concepts proposed by previous work at Botuverá (Cruz et al., 2005, Cruz et al., 2006, Cruz et al., 2007) as well as produced new ideas and data that are useful in the analysis of sample CR1 by using multiple speleothems.

Samples collected from Botuverá Cave and examined by Wang et al. (2006) provide a record for the most recent 90 kyr (Wang et al., 2007) as well as the past 10 kyr and 36 kyr (Wang et al., 2006) with some detectable hiatuses. These records are valuable for the interpretation and validation of CR1 data because Botuverá Cave and Cristal Cave are geographically close (~ 300 km). Sample BTV3A provides a stable isotope record
extending ~ 90 kyr without any detectable hiatuses and $\delta^{18}$O values ranging over 4‰ (Wang et al., 2007). Botuverá Cave samples analyzed by Wang et al. (2007, 2006) all display $\delta^{18}$O values that linearly track summer insolation, similar to previously discussed work by Cruz et al (2005). These records will be analyzed further in the Discussion section regarding possible correlations with CR1 $\delta^{18}$O and $\delta^{13}$C.

### 3.4 Stable Carbon Isotopes in Speleothems

When analyzing speleothem carbonate via mass spectrometry additional stable isotope data is produced alongside $\delta^{18}$O. Carbonate contains both oxygen and carbon allowing for the generation of concordant $\delta^{13}$C values. However, the $\delta^{13}$C of speleothems is useful only if the contribution of all possible influences on its composition can be accurately and precisely identified. For the case of Bt2 and work by Cruz et al. (2006), it was appropriate to state that variability of $\delta^{13}$C was due primarily to changes in local moisture availability and temperature. This was a reasonable determination to make because all other factors had been strongly discredited i.e., changes in the bedrock dead carbon fraction, large scale vegetation changes (at least over specified time intervals) and in-cave kinetic fractionation effects had all been determined to have minimal impact of speleothem $\delta^{13}$C. Yet it is important to recognize that not all studies of speleothem $\delta^{13}$C are so clearly defined and in cases where all variables are seemingly known and accounted for, $\delta^{13}$C can still prove to be an unreliable.

Work by Baker et al. (1997) focused on $\delta^{13}$C of 41 actively growing speleothems sampled near Yorkshire, England. The location of this study is crucial, as the climate and vegetation of the area has remained largely unchanged since the late Holocene and contains exclusively $C_3$ type vegetation. Due to the predominance of $C_3$ plants, the
expected range of $\delta^{13}C$ for speleothem calcite is between $-12$ to $-6$‰ (Baker et al., 1997). A degree of variability is to be expected for 41 samples, however Baker et al. (1997) noted that ten percent of speleothems sampled have $\delta^{13}C$ values greater than $-6$ per mille and that the entire sample set had a relatively large range ($-8.06$ ‰ ±$1.38$ ‰ ). Not only were elevated values noted in those speleothems selected and analyzed for this study, but a review of the available literature by Baker et al. (1997) reveled that approximately 75% of flowstone samples and 57% of stalagmite samples from the British Isles displayed elevated $\delta^{13}C$. Variability of stalagmite $\delta^{13}C$ collected in the British Isles was attributed to three possible processes according to Baker et al. (1997) and includes such factors as kinetic fractionation as CO$_2$ degasses from solution, degassing of groundwater in the soil zone before infiltrating the cave and short residence times of water in the soil zone preventing equilibrium between the soil water and soil CO$_2$.

3.5 Sedimentary Records

3.5.1 Cariaco Basin Inorganic Chemistry

Oftentimes, one of the goals of a regional paleoclimate reconstruction is to construct a record that is not only accurate but is also in agreement with other geographically close or process related proxy records. In the case of paleoclimate studies in southeastern Brazil, there are currently few non-speleothem proxies readily available. Although not geographically close to southeastern Brazil, the Cariaco Basin provides a comparable record of climatic processes in southeastern Brazil that offers the opportunity for comparison that warrants further investigation.
Located off the northern coast of South America, the anoxic Cariaco Basin provides an excellent opportunity to examine climatic change over northern South America through the analysis of varved sediments. When precipitation is high over northern South America there is a corresponding increase in sediment (and therefore titanium) runoff into the Cariaco Basin. Thus, high sediment Ti concentrations correspond to generally wet periods while low sediment concentrations correspond to relatively low precipitation periods.

Although sediments from ODP sites have been investigated using a variety of techniques, perhaps the most revolutionary method was pioneered by Haug et al. (2001). Through the use of a profiling x-ray fluorescence scanner, Haug et al. (2001) was able to analyze Cariaco Basin sediments at sub-decadal (~ 4-5 y) resolution. The resultant 14 kyr record allowed for a reconstruction of Intertropical Convergence Zone (ITCZ) migration through the Holocene. Through analysis of titanium concentrations in sediment cores, it was determined that drier conditions existed over much of northern South America beginning ~ 5.4 kyr ago and high amplitude fluctuations with corresponding precipitation minima are detectable at 3.8 to 2.8 kyr ago (Haug et al. 2001). This provides valuable insight for speleothem studies in southeastern Brazil because it may offer evidence for teleconnections in northern South America, the northern hemisphere and Pacific based climate effects (such as ENSO).

Perhaps the most important finding of Haug et al. (2001) is that the mean latitudinal position of the ITCZ is variable and that ITCZ position is the primary determinate of Ti and Fe variations at ODP site 1002. This chemical variation is governed by increases in precipitation and wind-driven upwelling that take place beneath
the oceanic ITCZ. The fact that interannual migration of the ITCZ establishes such a strong signal in Cariaco Basin sediments helps to establish correlations with other paleoclimate proxies. Haug et al. (2001) cites sediment records from Lake Titicaca and pollen records from the southern Amazon margin as establishing an anticorrelation in seasonality of precipitation resulting from the southern migration of the ITCZ. This will prove to be a valuable finding and will offer a chance to explore further anticorrelation between Cariaco Basin sediments and southeastern Brazil stalagmite $\delta^{18}O$ records, which will be discussed later in this report.

Later work by Haug et al. (2003) focused on obtaining bi-monthly resolution of Ti and Fe concentrations from ODP sediment cores 1002C and 1002D with the aid of an X-ray fluorescence scanner. This more recent work by Haug et al. (2003) is similar to earlier work by Haug et al. (2001) in that it relies on sediment Ti and Fe concentrations in order to infer regional aridity and the mean latitudinal position of the ITCZ. Perhaps the most important aspect of the more recent publication is that it offers a sub-annual record of latitudinal ITCZ over northern South America that can be directly applied to a historical event, in this case the collapse of the Maya civilization. The findings of Haug et al. (2003) are not necessarily vital to this report, but the fact that sub-annual resolution is possible in Cariaco Basin sediments and the data provided offers a comparable record with which to examine alongside southeastern Brazil $\delta^{18}O$ for anti-correlation.

### 3.5.2 Lake sediment and pollen records

In the search for comparable paleoclimate proxies in southeastern Brazil, it is appropriate to devote some attention to sedimentary pollen records. Pollen records are desirable because they offer an opportunity to examine records of climatic change on
spatial and temporal scales similar to those offered by speleothems. Unfortunately, pollen analyses are relatively rare in southeastern Brazil and although Behling et al. (1997) provides a record dating between 18,000 and >48,000 $^{14}$C yr BP, the time interval covered is not applicable to this report. However, Behling (2002) offered a synthesis report of sedimentary pollen analysis of southern and southeastern Brazil. According to the record presented by Behling (2002) the most recent 1 kyr BP have been the wettest since the LGM as inferred from cores retrieved at Lago do Pires (which is nearly 1000 km northeast of Cristal Cave). It is mentioned that there is no similar wet period observed during similar time intervals at other locations in South America, i.e. equatorial regions. Although there is a possibility that this record is anomalous, Behling (2002) feels that this is unlikely. It is also possible the $^{14}$C dating has led to an inaccurate chronology of cores examined by Behling (2002). Though this may very well be the case, it still stands that the wettest period (relatively) since the LGM in southeastern Brazil occurred during the last 1 kyr BP.

Perhaps even more useful than the pollen derived record of precipitation in southeastern Brazil, the history of moisture availability in the Amazon Basin provides a record for one of three major global convection centers in addition to tropical Africa and the tropical Western Pacific (Webster et al., 1983). More specifically in regards to precipitation in southeastern Brazil, Amazon Basin moisture availability exerts much control on the character of precipitation falling in that region. It is important to remember that much of the precipitation falling over southeastern Brazil during the summer monsoon season is not derived locally, instead it is sourced from the Amazon basin.
Selecting lakes appropriate for reconstructing moisture availability of the Amazon Basin is difficult, as many lakes have existed for a relatively short time and have often not existed continually. One such exception to this trend is Lake Titicaca, located in the northern Altiplano, between the western cordilleras of the tropical Andes. Work by Baker et al. (2001) examined sediment cores recovered from the lake in order to construct a ~25 kyr record of tropical precipitation in South America. Late Titicaca is important because it is one of the only large fresh water lakes in South America and precipitation anomalies in the lake can often be correlated with climate anomalies in the Amazon Basin.

Baker et al. (2001) used multiple proxies to examine paleoclimatic change in Lake Titicaca, focusing on magnetic susceptibility, diatom and foraminifera concentrations, stable carbon isotopic composition of total organic carbon and weight percent of calcite in order to constrain lake level fluctuations. As part of the investigation, Baker et al. (2001) has positively correlated lake level to instrumental precipitation records. Although the record constructed by Baker et al. (2001) spans the last 25 kyr BP, only data pertaining to the late Holocene is relevant to this report, although it should be noted that the lowest lake level for the past 25 kyr occurred during a period 6-5 kyr BP. It was determined that after lake level reached its lowest level during 6-5 kyr BP, lake level began to rise at ~4.5 kyr. Although the sedimentary record at Lake Titicaca provides a fairly long record, it does not have sufficient breadth or resolution to adequately describe the late Holocene. Fortunately, sedimentary records from Lago Wiñaymarka, a sub-basin of Lake Titicaca, provide a more detailed lake level history (Abbott et al., 1997). Abbott et al. (1997) found four significant low stands in lake level, all of which occurred
abruptly over a period of ~100-200 years. These low lake levels are displayed graphically in Figure 5 and most notably show low lake levels at 700, 1800, 2300 and 3000 cal yr. BP. Within the sedimentary record, these low stands are marked by erosional surfaces and are the result of lake level changes greater than 22 meters during the past 3.5 kyr BP (Abbott et al., 1997). Abbott et al. (1997) suggest that the relative abruptness with which these lake level shifts occur is likely due to the fact that changes in atmospheric circulation are responsible for much of the variability encountered, but offer no further insights as to a possible mechanism.

Figure 5 - Schematic representation of Lake Titicaca Lake levels inferred from sediment cores taken in the adjoining Lago Wiñaymarka basin. Figure modified after Abbott et al. (1997).
Lake Titicaca and its associated sub-basins provide a valuable record for reconstructing Amazon Basin moisture availability primarily due to the lake’s geographic location. Situated on the Junin Plain between the Cordillera Oriental and Cordillera Occidental of the Andes mountain range, Lake Junin also provides an excellent opportunity to examine proxy records for lake level, much the same way as Lake Titicaca. Work by Seltzer et al. (2000) focused on the examination of stable carbon and oxygen isotopes of authigenic calcite trapped in lake sediments in order to constrain changes in $\delta^{18}O$ and relate that to the precipitation source moisture $\delta^{18}O$, temperature of calcite precipitation and the general hydrology of the lake basin. It should be noted that the primary source of moisture for Lake Junin is from easterly air masses that is transported to the lake during the austral summer (Johnson, 1976). Thus, precipitation falling at Lake Junin possibly represents conditions influenced by moisture availability in the Amazon Basin. The $\delta^{18}O$ of authigenic calcite in the lake is thought to be governed principally by available moisture at the lake; during relatively wet periods there is less evaporative enrichment that leads to decreased $\delta^{18}O$ values of authigenic calcite (Seltzer et al. 2000). The conclusions reached by Seltzer et al. (2000) were similar to other workers in regards to the fact that aridity in the South American tropics and sub-tropics was prevalent during the early Holocene, but the middle and later Holocene became increasingly moist. Seltzer et al. (2000) adds to these arguments by concluding that the general trend of Lake Junin $\delta^{18}O$ values is closely related to January insolation at 10° S which in turn, is positively correlated with increased convection to the east and corresponding development of the Bolivian High, thought to be highly sensitive to changes in insolation.
3.6 Isotopes and Global Circulation Models

In order to form a baseline for global scale isotope distribution, the measurement of stable isotopes in precipitation was begun in earnest during the early 1960’s by the International Atomic Energy Agency (IAEA) (Dansgaard, 1964). As part of this program, measurements of $^{18}$O, $^2$H and $^3$H were made monthly at over 800 meteorological stations throughout the world, a practice that continues today. Some of the first analysis of IAEA-WMO data was synthesized by Dansgaard (1964) and addressed fundamental concepts such as the effect of latitude and altitude on the isotopic composition of precipitation, as well as the possibility of an “amount effect” in the tropics and subtropics whereby the amount of precipitation is inversely correlated to the $\delta$H or $\delta$O of the precipitation. Dansgaard (1964) also addressed precipitation stable isotope data that displayed seasonal variability as well as variability associated with altitude and temperature effects. Addressing that fact that variability occurs both on seasonal and spatial scales helped lead to further development of ideas pertaining to the overall role stable isotopes in precipitation play as a tracer.

These measurements have enabled the analysis of short term processes in the hydrosphere through the tracking of the tritium ($^3$H) created during atmospheric nuclear weapons testing as well as the construction of the meteoric water line (Figure 3). Spatial distribution of sampling stations is relatively low on a global scale, yet the distribution is such that much of the world is represented. Although initial measurements by the IAEA were focused on determining the spatial and temporal variability of isotopic changes in precipitation, many modern researchers have used IAEA data in order to validate global circulation model (GCM) data.
Stable isotope precipitation data was used extensively by Vuille and Werner (2005) to validate model output for an atmospheric general circulation model (AGCM). This is a worthwhile approach to take, as model validation ultimately leads to more accurate and precise models as well as the potential for more realistic hypothetical atmospheric circulation and isotope transfer mechanisms. Vuille and Werner (2005) used ten summers worth of data from IAEA-GNIP stations in South America to validate model output. Since data from the IAEA-GNIP is temporally sparse, rainfall $\delta^{18}O$ values from meteorological stations were combined with annually resolved $\delta^{18}O$ from Quelccaya, Huascarán and Sajama tropical Andean ice cores in order to construct a more complete data set for South America.

It should be noted that this was done in order to validate model output, not as an initial source of data for the model. For this particular work, Vuille and Werner were able to more thoroughly define aspects of the South American Southern Monsoon (SAMS) as well as possible teleconnections to ENSO.
4.1 Introduction

Speleothem is a broad term for all cave formations and includes such common cave features as stalagmites, stalactites and flowstone. Many speleothems are similar in that they are made of calcium carbonate precipitated as CO$_2$ degasses from a super saturated solution in a cave creating features that take on a multitude of forms. Although it is possible for stalactites to provide useful data (Zhou et al., 2007, de Cisneros et al., 2004), typically only stalagmites are used for paleoclimate reconstruction due to their stable growth geometry.

The deposition of CaCO$_3$ in a subsurface environment is a process that relies not only on activity within the cave itself, but also processes on and near the surface. The most common way for speleothems to form requires meteoric precipitation to come in contact with CO$_2$ in the atmosphere and/or soil before entering the subsurface. This a process represented by the following equations:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3
\]
(Equation 1)

\[
\text{H}_2\text{CO}_3 + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-
\]
(Equation 2)

\[
\text{Ca}^{2+} + \text{H}_2\text{CO}_3^- \leftrightarrow \text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O}
\]
(Equation 3)
Typically, bacterial respiration in the soil zone results in soil pCO$_2$ being as much as ten times higher than in the atmosphere (Faure, 1998). As such, most of the CO$_2$ incorporated into infiltrating water is derived from the soil, not the atmosphere (process shown in Equation (1)). Once CO$_2$ is incorporated into meteoric precipitation, the water moves through the soil and into the epikarst zone where the limestone bedrock and unconsolidated soil layer meet (represented by Equation (2)). Much dissolution occurs here due to the fact that aggressive infiltrating waters have not had previous contact with limestone (Palmer, 2007). As water infiltrates deeper into the underlying bedrock it looses much of its solutional aggressiveness and the rate of dissolution decreases rapidly as the infiltrating water becomes supersaturated (Palmer, 2007). Once this supersaturated solution enters the cave environment it quickly degasses, loosing CO$_2$ because although the pCO$_2$ of the cave atmosphere is much higher than that of the surface atmosphere, it is significantly lower than the pCO$_2$ in the soil zone. As CO$_2$ is lost from solution, CaCO$_3$ is precipitated in-situ, shown in Equation (3). If water infiltrates at a single point stalactites may form on the cave ceiling, if some CaCO$_3$ remains in solution then a stalagmite may precipitate on the cave floor. This entire process is represented schematically in Figure 6.
Figure 6 - Schematic representation of a typical cave and karst setting. Label (1) shows the soil layer while label (2) indicates underlying bedrock. Labels (3) and (4) show typical orientation of stalactites and stalagmites, respectively.

Speleothems are suitable for climate reconstruction for several reasons, principally because caves represent an environment that is relatively stable and unchanging in comparison to the surface. It is this unchanging background upon which variations in the climate of the surface are recorded. Speleothems which form in this environment most often record changes related to surface conditions and as an approximation, it is possible for speleothems to begin forming and recording this information once a cave passage has reached a traversable size. Whether or not a speleothem may grow continuously for the entire life of a cave (i.e. when the overlying bedrock is removed by surface and/or in cave processes) is unlikely but it is probable that the cave environment will remain stable as the surface experiences large climatic
fluctuations. Caves tend to reflect average surface conditions with factors such as in-cave temperature reflecting the average of the local air temperature (Hill and Forti 1997). As such, signals of large magnitude fluctuations of surface conditions are dampened within the cave, and are recorded in their unmodulated form in the speleothem.

The fact that speleothems record some manner of climatic signal has been recognized since the late 1960’s (Hendy and Wilson 1968). As previously noted, speleothems are suitable for paleoclimatic reconstruction because they form in a relatively stable environment over several tens of thousands of years. It is also important to recognize that one of the advantages of using speleothems as paleoclimate recorders as opposed to ice or sediment cores is that speleothems can be reliably dated using U/Th disequilibrium methods. Speleothems also have a relatively large-scale distribution with ~10 to 20% of the Earth’s surface area covered by karst (Palmer, 1991).

4.2 Speleothems as paleoclimate proxies

Several lines of paleoclimatic data can be gleaned from speleothems including the one foremost for this investigation, isotopic composition of meteoric precipitation. Speleothems record the stable isotopic makeup of local precipitation and isotopic composition that is largely the result of variation in precipitation intensity and moisture source location. This information helps to form the basis for most of the hypotheses posed during this research.

It is also important to note that speleothems have the potential to be reliable recorders of generally wet or dry periods (Polyak, 2001). During wet periods, there is typically more meteoric water infiltration into the cave and correspondingly more calcite deposition. It is possible for stalagmites found in caves located in regions with strong
seasonality to exhibit annual growth layers and occasionally the thickness of these annual rings can be correlated to climatic variability. During generally wet periods, increased water infiltration results in increased drip rates that frequently correspond with increased calcite precipitation and thicker growth layers. Generally wet periods result in less water infiltration and correspondingly slower drip rates with less calcite precipitation resulting in thinner growth layers. This relationship helps form relative relationships for wetter/drier conditions and has not yet been quantified, although techniques for determining the relative abundance of infiltrating meteoric precipitation have been presented (Fairchild and McMillan 2007). Techniques that rely on layer thickness measurement and counting may hold potential as a less expensive and faster analysis than oxygen isotope investigations as layer thickness counting and measurement can be done using ordinary optical microscopy techniques.

As is the case with most developing techniques, this tool must be used with caution. In caves that experience extremely wet conditions it may be possible for the influx of water to be so voluminous and rapid that corresponding large amounts of calcite deposition may not possible. It is also likely that caves located in areas with strong seasonality will also be prone to seasonal flooding. Once a speleothem is submerged underwater calcite can no longer be deposited via sub-aerial drips. Instead, calcite may be precipitated evenly around the entire speleothem. Conversely calcite may even be dissolved from the speleothem depending on the water chemistry. It may be said that changes such as those previously described are simply very large amplitude changes instead of seasonal or interannual changes that are often noted in layer thickness studies. The effect of extremely wet conditions (i.e. flooding) is not always apparent in the field
and care must be taken to avoid speleothems that may have been modified by post depositional flooding. Fortunately samples that have experienced flooding which results in a change in morphology are often identifiable in the lab after slabbing the sample but before age determination.

There are several other techniques which can be utilized for speleothem paleoclimate analysis which may hold promise, including the analysis of fossilized mites and alternation between calcite and aragonite layers within individual stalagmites (Polyak, 2001). It is thought that changes in the species distribution of well preserved fossil mites may be a broad indication of climate change and that alternation between calcite and aragonite layers indicate changes in aridity in a fashion similar to that of layer thickness. However the precipitation of aragonite is often a sign of increased evaporation within the cave as opposed to on the surface (Hill and Forti 1997). Since caves reflect average surface conditions, increased evaporation within the cave is thought to correlate with increased aridity of the surface environment.

Techniques used to extract paleoclimate information from speleothems are varied in methodology, precision and accuracy. One of the most reliable and widely used techniques applied to speleothems is stable isotope analysis. Researchers have been using both carbon and oxygen isotope studies to piece together climatic histories since at least the late 1960’s (Hendy and Wilson 1968). However, stable isotope analysis of speleothems is not without potential pitfalls. One of the greatest issues of speleothem based stable isotope studies is in-cave fractionation. However, even though kinetic isotope fractionation is possible in stalagmites, the effect is minimal. In addition the observed variation in $\delta^{18}$O is typically too great to be purely the result of fractionation
effects due to in-cave temperature change. Any significant change of in-cave temperature would likely be the result of dramatic surface temperature fluctuations, ones that would most likely occur on time scales longer than those encompassed by most stalagmites (generally no more than several hundred thousand years).

It is generally appropriate to assume that in-cave fractionation is not be a factor in controlling $\delta^{18}O$ of most speleothems, however it is best to avoid such fundamentally critical assumptions. To test whether or not kinetic or evaporative fractionation has occurred it is best to sample for $\delta^{18}O$ along a single growth layer, a process known as the “Hendy Test” (Hendy and Wilson 1968). If adverse effects are present and detectable, $\delta^{18}O$ composition will change along the layer. Variation not occur in an ideal case as relatively constant in-cave temperature and high humidity make it unlikely for kinetic or evaporative effects to dominate. For stalagmite based paleoclimate reconstruction over periods of several thousand years, it is more than likely that the overriding influence on $\delta^{18}O$ is the $^{18}O$ of infiltrating meteoric precipitation.

4.3 U/Th Dating of Speleothems

Perhaps the greatest advantage of using speleothems for paleoclimate reconstruction is that it is possible to establish an absolute chronology for samples using uranium series methods. This allows for a concise and accurate chronology to be established that relies on chemical parameters, not just simple layer counting or the physical distance of a sub-sample from the most recent growth surface. Uranium series methods had been used on carbonates since the 1950’s and the first successful dating of a speleothem was done in the 1980’s using newly developed mass spectrometry techniques (Dorale et al., 2004). Since the 1980’s, techniques have advanced to the point that it is
now possible to precisely and accurately date speleothems ranging in age from a few tens to 600,000 years old (Dorale et al., 2004).

Radiometric dating of speleothems is possible in part because of the extreme fractionation that U and Th undergo in surface water systems. Solubilities of these two elements vary greatly, with U extremely soluble as the UO$_2^{2+}$ ion and Th extremely insoluble as the Th$^{4+}$ ion. This dichotomy leads to an abundance of U dissolved in groundwater. As uranium rich groundwater moves through a karst system uranium is incorporated into the crystal lattice of any carbonate precipitated from infiltrating waters; in an ideal situation the amount of Th entrained in the crystal lattice is negligible. As $^{238}$U decays to its intermediate daughter products ($^{234}$U, $^{230}$Th, $^{206}$Pb), the growth and decay of these daughters can be used to date the initial fractionation event, which in the case of calcite speleothems is the initial precipitation of CaCO$_3$. Since the half-life ($t_{1/2}$) of $^{238}$U is $\sim 4.5$ Ga, secular equilibrium with intermediate daughter products such as $^{230}$Th is easily obtained. It is important to note that any recrystalization of the speleothem will result in an effective “reset” of its internal clock.

Once U and Th isotopes are separated by virtue of their differing solubilities, U/Th disequilibrium dating methods may be reliably applied to the resultant carbonate. If the system remains closed then the following equation can be used to determine time since initial fractionation:

$$\left[ \frac{^{230}\text{Th}}{^{238}\text{U}} \right] = 1 - e^{-\lambda_{230}T} + \left( \frac{\delta^{234}\text{U}[m]}{1000} \right) \left( \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left( 1 - e^{(\lambda_{234} - \lambda_{230})T} \right)$$

Equation (4) (Dorale et al., 2004)
The most accurate ages are obtained when initial concentrations of $^{230}$Th are known and the post depositional calcite remains closed to any exchange of uranium, thorium or protactinium, a situation which accurately describes most speleothems (Dorale et al., 2004). It is often difficult to select a speleothem in the field with any certainty that will contain coherent data, even though workers have sought to refine collection protocols (Frappier, 2008).

Once an absolute chronology is established, there are several guidelines that can be followed in order to help determine if the resultant ages are accurate. Evidence for closed system conditions are often noted by a close concordance between $^{230}$Th and $^{231}$Pa derived dates. (Dorale et al., 2004). There should also be an apparent stratigraphic agreement in the age of subsamples; calcite near the bottom of the stalagmite should be older than calcite near the top. This seems a simple distinction to make, however when many physically and chronologically close ages are determined it can be easy to overlook a discordant age. Over the last few decades it has become apparent that the best speleothems for accurate chronological reconstruction are typically those that are comprised of dense calcite and are chemically closed to the introduction or loss of parent and/or daughter isotopes.
4.4 Oxygen Isotopes

Paleoclimate reconstruction through the use of oxygen isotope ratios in speleothems is possible due to the inherent mass differences between the three stable isotopes of oxygen: ¹⁶O, ¹⁷O and ¹⁸O. Of the three, ¹⁷O is the least common and is rarely observed in meteoric precipitation. Oxygen-16 is the most common (99.762% abundance) and ¹⁸O is the second most common (.200% abundance) (Faure, 2005). Water formed by bonding with these isotopes results in H₂O molecules with differing masses reflecting their isotopic makeup. The resulting mass difference forms the basis for characteristic differences in the physical behavior of water molecules that incorporate either ¹⁶O or ¹⁸O. This leads to markedly different behavior in phase transitions, biological processes and chemical reactions. This phenomenon is due largely to the influence of isotope mass on the mechanics of bonding. For example, H₂O molecules formed incorporating ¹⁶O have a higher vibrational frequency than H₂O molecules utilizing ¹⁸O. Vibrational frequency (ν), is a characteristic that is expressed in the equation:

\[ E = \frac{1}{2} h \nu \]

Equation (5)

where E is energy and h is Planck’s constant. In the case of a diatomic molecule, replacing one of the light isotopes with a heavy isotope of the same element causes ν to decrease. This results in an overall decrease in the energy of the molecule and causes molecules containing the heavy isotope of an element to be less reactive than molecules
formed with the corresponding light isotope. This behavior forms the basis for mass
dependent fractionation. Although there are other types of stable isotope fractionation
resultant from biologic or chemical activity, they are not as important to speleothem
based paleoclimate research as mass dependant fractionation.

As shown via Equation 5, different isotopic masses yield different molecular
energies. In a liquid this causes similar molecules of differing isotopic composition to
have unique vapor pressures. For example, in a mixture containing both common stable
isotopes of oxygen, $^1\text{H}_2^{16}\text{O}$ will evaporate preferentially to $\text{D}_2^{18}\text{O}$ and correspondingly,
$\text{D}_2^{18}\text{O}$ will condense from vapor before $^1\text{H}_2^{16}\text{O}$. This discrepancy in behavior of
seemingly similar water molecules leads to the formation of the meteoric water line,
whereby changes in the isotopic composition of meteoric precipitation correspond closely
to changes in distance from the moisture source location.

Changes in isotopic composition also result from the intensity of convective
upwelling, a critical measure for this investigation. In order to create a meaningful,
standardized measure of the ratios of isotopically diverse compounds, the “delta” notation
is used. In this notation, the isotopic composition of a compound is given in reference to
some standard material. Delta notation is not only used for oxygen isotope studies it is
commonly used to describe other stable isotope systems as well. In the case of oxygen
isotope systems, the standard for the isotopic composition of water is Standard Mean
Ocean Water (SMOW) and for calcite PDB, in reference to a Cretaceous belemnite from
the Pee Dee formation in South Carolina that was originally used as the standard
material. Since both original standard materials have been entirely consumed, the
International Atomic Energy Administration (IAEA) has issued “synthetic” materials that
closely reflect the isotopic composition of the original standard material. The current
substitutions for SMOW and PDB are referred to as VSMOW and VPDB. Since the
isotopic composition of the new reference material and the original material is not
identical this fact should be noted when dealing with older literature.

In order to discuss relative isotopic values, the terms “enriched” and “depleted”
are used. These descriptors can be used to qualitatively describe the changes in the
concentration of a particular isotope in any system in relation to the standard material.
Although qualitative terms are helpful when describing a general situation it is typically
necessary to use quantitative terms to best describe isotopic change. In order to do that
the delta (δ) notation is used whereby:

\[
\delta^{18}O = \left( \frac{\frac{^{18}O}{^{16}O_{\text{sample}}}}{\frac{^{18}O}{^{16}O_{\text{standard}}}} \right) \cdot 1000
\]

Equation (6)

The resultant values are given the unit of per mille (‰). Equation 6 effectively
quantifies oxygen isotope ratios and stating that a sample is enriched or depleted must be
made in reference to the light or heavy isotope. When stating that a sample has a higher
(more positive) \(\delta^{18}O\) value than another, it is said to be enriched in \(^{18}O\) relative to \(^{16}O\)
while a lower (more negative) value is said to be depleted in the heavy isotope (in this case $^{18}$O) relative to $^{16}$O.

4.5 Carbon Isotopes

The interpretation of speleothem $\delta^{18}$O is fairly straightforward; values are often in strong agreement with moisture source and/or moisture amount (the amount effect). However carbon isotopes, which are often measured synchronously, are much more difficult to interpret. This is primarily due to the availability of carbon in the global reservoir and the unique isotopic signature that each reservoir has. Changes in vegetation are sometimes invoked in order to best describe the changes in $\delta^{13}$C, but for most speleothem records on the order of several hundred to several thousand years, large magnitude changes are unlikely. The most likely indirect driver of change is a fluctuation in rainfall and local aridity which will influence rates of organic production and decay in addition to calcite saturation conditions of infiltrating waters (Williams et al., 1999).

The supply of carbon for the incorporation into speleothems is essentially limited to two sources: dissolved inorganic carbon (sometimes referred to as the dead carbon fraction) in limestone and CO$_2$ supplied by plant respiration and decomposition (Hendy, 1971). The isotopic signature of the dead carbon fraction and that supplied by CO$_2$ is unique as is the $\delta^{13}$C of carbon supplied by CO$_2$. The $\delta^{13}$C values of CO$_2$ supplied by plant respiration and decomposition are strongly influenced by the makeup of the vegetation that inhabits land above the cave. Plant communities can be roughly divided into those falling into C3 or C4 categories. C3 vegetation is primarily composed of plants typically associated with cool moist climates, such as trees, shrubs, and grasses while C4 vegetation is typically comprised of dry season grasses (Denniston et al., 2000).
CHAPTER 5

METHODS

5.1 Introduction

Stalagmite CR1 was collected while active during June 2007 from Cristal Cave, São Paulo state, Brazil. After collection, CR1 was cut and polished along its vertical growth axis allowing for easier identification of growth layers and sub-sample collection on the resultant flat, polished surface. The cut surface of the sample was otherwise left untreated. Only one half of the sample was used for stable isotope analysis and age determination while the other half was archived.

5.2 Sampling for Stable Isotopes

Sample collection for stable oxygen and carbon isotope analysis was performed using a Sherline micromill equipped with a digital XYZ axis readout enabling sample collection at 100 µm intervals. These samples were analyzed for stable carbon and oxygen isotopes using a Thermo Finnegan Delta+XL mass spectrometer coupled to a Kiel III carbonate preparation device. The Kiel III combined with the Delta+XL allows for the analysis of carbonate samples on the order of micrograms and with a precision ± .05 ‰, however the maximum attainable resolution is largely dependant on speleothem growth rate and the precision and accuracy of the Sherline micromill. Currently, the maximum attainable sampling resolution with this mill is 50 µm. For CR1, there are two distinct but similar growth rates observed which allow sampling at either near annual or sub-decadal resolution (generally <5 yr). Because of this, the most recent ~750 years were sampled at nearly annual resolution while all prior periods were sampled at nearly decadal scale resolution.
5.3 Age Model Construction

An age model of CR1 growth history was constructed using dates provided by fifteen subsamples taken along the stalagmite’s vertical growth axis. These subsamples were taken at approximately regular intervals with the upper ~14 cm sampled every ~1.5 cm while the remainder was sampled every ~3 cm. The sampling resolution was higher in the upper ~14 cm of the sample in order to provide a more detailed growth history of the most recent deposition. Subsamples were collected using similar techniques and methods as those collected for stable isotope analysis. One notable difference is that the amount of material required for the U/Th disequilibrium dating technique is much greater and necessitates ~200 milligrams of sample as opposed to approximately one thousand micrograms for stable isotope analysis.

It should be noted that while samples for stable isotope analysis are assumed to be “point” samples and that those required for U/Th age determination are much larger and are taken along a single growth layer. This leads to the possibility of error due to the fact that the amount of material required for U/Th dating necessitates a relatively large drill bit that has a diameter larger than the thickness of a single growth layer. Thus when collecting a sub-sample, several growth layers are sampled even though an age is only assigned to a single depth (and therefore a single growth layer). This results in an averaging of ages for several growth layers, a problem that is most significant in slow growing speleothems where many growth layers are sampled in a single sub-sample. Since several growth layers were averaged during sampling of CR1, ages are assigned to the X-axis center point.
Subsamples provide discrete ages along the growth axis of CR1, yet in order to determine the age of calcite between those points it was necessary to construct an interpolated age model. To do this, the age of each sub-sample was plotted against sub-sample depth for the entire length of the stalagmite. These data points provided a known set of markers with which to proceed with interpolation. The basis of this technique relies on the fact that when plotted, two adjacent dates (subsamples) will yield a line with a known slope and y-axis intercept and an equation for that line in slope intercept formula. The calculated slope and y intercept for each pair of data points is then applied to points along the stalagmite with known depth but unknown age. This process is applied along the entire growth axis of the sample and eventually yields interpolated ages between absolute ages as well as interpolated growth rates along various points in the sample. This method is often referred to as “linear interpolation” and is frequently used to construct age models for speleothem studies.

5.4 Oxygen Isotope Measurements

Speleothem based paleoclimate studies rely heavily on stable oxygen isotope ratios measured via atomic mass spectrometry. This investigation is no different and the majority of the data generated for this study is the result of mass spectrometry analysis. The mass spectrometry of carbonates is possible because of the elemental composition of the material and the inherent mass differences between isotopes.

The Delta +XL mass spectrometer used for this investigation is a gas source unit requiring that the sample carbonate be converted to a gas via the Kiel III carbonate preparation device. This machine allows for the analysis of carbonate on the order of micrograms and essentially works by reacting carbonate with phosphoric acid which then
releases CO₂. This resultant CO₂ is then fed through a cold finger that is cooled by liquid nitrogen and helps to remove any water vapor entrained in the CO₂ gas. The resultant cold, dry CO₂ is fed into the mass spectrometer.

As previously mentioned, the Delta +XL is a gas source unit, which makes the analysis of CO₂ liberated by the reaction of CaCO₃ and H₃PO₄ possible. The CO₂ released contains both carbon and oxygen isotopes and the Delta +XL is able to measure both isotopes at the same time. Since mass spectrometry plays such a critical role in this investigation, it is important to understand the fundamentals of the technique. The following description and explanation of stable isotope mass spectrometry is adapted from Faure (2005).

The mass spectrometer works by separating atoms based solely upon their mass. In the case of carbonates, this is accomplished by feeding gas from the Kiel III into the mass spectrometer through a small orifice while the sample chamber is under vacuum. The gas is then ionized by electron bombardment which results in positively charged atoms. Once the gaseous atoms are ionized, they are formed into a beam and accelerated down the flight tube by electromagnets. As ions move down the flight tube they are deflected by an electromagnet along a semi-circular pathway. This leads to the separation of ions according to their mass i.e., heavier ions are deflected less than lighter ions. After passing near the electromagnet, ions move down an analyzer tube before reaching an ion collector. These collectors typically consist of one or more Faraday cups positioned behind a slit plate. At this point, ions are positioned differently according to their mass and as such, some ions will go through the slit plate and strike the Faraday cup, while others will collide with the grounded slit plate. When analyzing compounds, the
electromagnet is manipulated such that beams of different ions alternately strike the slit plate or Faraday cup. The Faraday cup is able to register a signal depending on the number of ions striking it. The composite signal forms the mass spectrum of each element, with peaks representing mass-to-charge ratios identifying each element and the high point of each curve representing the relative abundances of each isotope.
CHAPTER 6
RESULTS

6.1 Introduction

The use of proxies to reconstruct ancient climates is often a multi-pronged approach, with a variety of parameters frequently extracted from a single sample in order to construct a coherent and reliable record. Stalagmite CR1 is no exception and a variety of techniques have been used to yield a record of climate in southeastern Brazil. The construction of an accurate age model for CR1 is crucial as it places $\delta^{13}$C and $\delta^{18}$O values in an absolute temporal framework. A growth model for CR1 was constructed using a series of sub-samples collected along the stalagmite’s growth axis that were subsequently dated using U/Th disequilibrium techniques. The fact that the age model for CR1 provides extremely accurate ages allows for the direct comparison between CR1 $\delta^{18}$O, $\delta^{13}$C and instrumental precipitation values from geographically close meteorological stations. The accurate age model also allows for a relatively precise comparison between CR1 and other proxies as well as a high degree of confidence when making general observations concerning features of the CR1 data set. To better quantify observations a variety of spectral, wavelet and cross correlation analyses were performed where appropriate.

6.2 Age model

An age model for CR1 was constructed using U/Th disequilibrium methods in order to determine the age of subsequent subsamples collected for stable isotope analysis (Figure 7). A total of 15 subsamples taken along the stalagmite’s growth axis (Figure 8) are used to constrain growth rates. Average error for all subsamples is $\pm$ 15 years with
individual errors ranging from 6 to 26 years. Linear interpolation between data points yielded an age model with two similar but distinct growth rates of .047 mm/yr for the most recent 279 years and .36 mm/yr for the remaining 3,821 years. Analytical errors are within 2$\sigma$ of the mean and the following decay constants were used for age determination: 9.1577 x 10$^{-6}$ yr$^{-1}$ for $^{230}$Th, 2.8263 x 10$^{-6}$ yr$^{-1}$ for $^{234}$U, and 1.55125 x 10$^{-10}$ yr$^{-1}$ for $^{238}$U (Cheng et al., 2000). The high precision of the CR1 age model is possible in part because of very low initial Th values, which average 172.5 ppt for all subsamples. A table summarizing the appropriate data is given in the Appendix.

When constructing age models and calculating individual dates for sub-samples it is important to differentiate between calendar year and years “before present” (BP) whereby “present” is typically defined as calendar year 1950. This practice is not necessary when presenting ages obtained via U/Th techniques since these materials are not affected by anthropogenically induced spikes in radiocarbon levels that occurred during the 1950’s. For this report, ages calculated for CR1 are either presented as calendar year or as years BP whereby “present” is June 2007, the date at which CR1 was collected while actively growing.
Figure 7 - Age model for CR1. Red lines represent linearly interpolated ages between individually dated subsamples. Note the extremely small dating errors and the relatively constant growth rate. See the Appendix for formulas used for linear interpolation between data points.
Figure 8 - Stalagmite CR1 with labels showing sub-sample location for age model construction.
6.3 Stable Isotope Record

Stalagmite CR1 was sampled at two different spatial resolutions in order to make the best use of available time and to avoid creating an unrealistically high resolution data set that exceeds the limits of sampling techniques. In accordance with the age model, CR1 was sampled at relatively high spatial and temporal resolution for the most recent ~ 96 mm (~ 750 years) of growth. During this interval, sampling was done at a spatial resolution of .10 mm which equates to an average temporal resolution of 1.8 years. The remainder of CR1 was sampled at a spatial scale of .20 mm which is equivalent to an average temporal resolution of 2.7 years.

The CR1 stable isotope record (Figure 9) has several trends and features that are evident with simple observations. Over the entire growth history of CR1 (~ 4.1 kyr) average $\delta^{18}O$ values gradually decrease ~1 ‰ until modern day. However, isotopic values do not remain constant and some large scale excursions persist for several hundred years. Positive excursions are noted at 3 kyr BP, 1.1 kyr and .7 kyr and generally last ~ 100 years. Significant negative excursions are much less frequent with only one excursion occurring between calendar years ~1450 - 1860 during the period commonly referred to as the “Little Ice Age” (LIA) (Bradley, 1999). During 4.1 kyr BP to .5 kyr BP variability of $\delta^{18}O$ is low, generally not exceeding 1‰. The most recent 700 years are marked with the greatest variability observed in the record with the range of $\delta^{18}O$ exceeding 3‰. Average values of $\delta^{18}O$ were highest during the most recent 175 years (~4.65‰ as opposed to -5.10‰ for the entire record).
Overall trends of δ¹⁸O are not consistent for the duration of the record and significant changes are marked appropriately in Figure 10.

The interpretation of speleothem δ¹³C is sometimes not as straightforward as that of δ¹⁸O yet it is still worthwhile to describe the entirety of the data set since δ¹³C values show significant variation throughout the CR1 record. Carbon isotope values for CR1 display trends that are similar in sign (direction of change) but slightly larger in magnitude than δ¹⁸O. Several large scale excursions and trends already noted in CR1 are present in records of both δ¹⁸O and δ¹³C including an ~2‰ excursion during the LIA as well as an overall increase in values leading towards modern day.

Figure 9 - Stable carbon and oxygen isotope values for CR1.
Figure 10 - CR1 \(\delta^{18}O\) values with significant trends labeled. (A) increase in \(\delta^{18}O\) of 1.3 ‰ towards modern day (B) decrease of 1.4 ‰ towards modern day (C) decrease of .8 ‰ towards modern day.

6.4 Correlation of speleothem \(\delta^{18}O\) and \(\delta^{13}C\)

Elimination of the possibility of in-cave fractionation and evaporative effects is a critical factor to address for all speleothem based paleoclimate studies. There are several methods used to test for the influence of these processes including the “Hendy Test” as well as presence of significant correlation between \(\delta^{18}O\) and \(\delta^{13}C\) for concordant subsamples. Results of a cross correlation plot of these values for CR1 is shown in Figure 11. The correlation coefficient for \(n = 1602\) samples is \(r^2 = .110\) indicating that speleothem \(\delta^{18}O\) and \(\delta^{13}C\) values are indicative of deposition under equilibrium conditions.
Figure 11 - Cross plot of $\delta^{18}O$ and $\delta^{13}C$ for CR1. Note $r^2 = .110$ for n=1602 points.
Another test of critical importance for the identification of disequilibrium conditions is the “Hendy Test”, whereby $\delta^{18}O$ and $\delta^{13}C$ are measured along a single growth layer. Ideally there should be little or no variation of stable isotope values along each layer. For CR1, the “Hendy Test” was performed at two locations along the stalagmite’s growth axis as shown in Figure 12. Although some variability along growth layers is noted, it is likely not large enough to indicate that kinetic fractionation has occurred.

Figure 12 - Hendy Test showing variation of $\delta^{18}O$ and $\delta^{13}C$ at two separate growth layers along the center axis of CR1.

6.5 Instrumental Precipitation Record

Several weather stations are located within ~50 km of Cristal Cave and offer the opportunity to examine instrumental rainfall amounts beginning in the late 1940’s. Data from station F5-007_3 in Eldorado provides daily rainfall amounts beginning in 1946. Notable trends include a gradual increase of ~ 250 mm in total yearly precipitation until
1982 and a corresponding maximum value of yearly total precipitation occurring in 1982. Precipitation data from station F5-042 in Iporanga is available from 1974 to 2004 and monthly averages indicate that the greatest rainfall in the region typically occurs during January and February while comparatively little precipitation falls during July and August (Figure 13). Although there are distinct wet and dry periods, most of the precipitation is evenly distributed throughout the year (Figure 14). It is notable that the increase in yearly total precipitation noted during the 1980’s is also apparent in records from Iporanga.

Figure 13 - Iporanga and Eldorado total annual precipitation. These stations are ~ 60 km apart and both record a notable increase in precipitation during the early 1980’s.
Figure 14 - Yearly average precipitation (1972 – 2004) at Iporanga weather station F5-042.

Figure 15 - CR1 stable isotope values plotted with instrumental precipitation records. Note the reversed $\delta^{18}$O/$\delta^{13}$C axis that helps emphasize an apparent “amount effect”.
As a first approximation, it appears as though CR1 δ¹⁸O broadly follows precipitation amounts (Figure 15). However, to better quantify any potential relationship between precipitation amount and CR1 δ¹⁸O values, a non-normalized cross correlation using FFT was applied. At a time lag of zero the correlation coefficient is $r^2 = -0.038$ but at 5.1 years it is $r^2 = 0.500$. Figure 16 better illustrates potential relationships between CR1 stable isotope values and instrumental precipitation amount by shifting δ¹⁸O and δ¹³C 5.1 years.

Figure 16 – Eldorado and Iporanga precipitation data with δ¹⁸O and δ¹³C shifted -5.1 years to better illustrate potential relationships between isotopic composition and precipitation amount. Note the reversed δ¹⁸O/δ¹³C axis that helps emphasize an apparent “amount effect”.
6.6 Wavelet Analysis

Identification of cycles in paleoclimate records is important not only to more fully describe the data set, but also to help identify possible forcing mechanisms. Wavelet analysis is one of the most useful tools for identifying cyclicity within time series and as such, the technique was applied to CR1 δ¹⁸O. Raw data was resampled (as required by the Matlab script used) at an evenly spaced interval of one year for the entire data set. This interval was selected because it does not degrade the original high resolution CR1 data set. Results of this analysis are shown in Figure 17 and indicate a significant (above the 95 % confidence level) periodicity of ~90 years concentrated at ~500 y BP and ~3000 y BP.

CR1 wavelet power is represented graphically in Figure 18. Individual panels describe the following: (a) normalized, detrended CR1 δ¹⁸О time series with x-axis values corresponding to year BP, (b) complete wavelet power spectrum using a Morlet wavelet with warm colors showing increasing variance at specified periods along the y-axis. Black lines enclose variance exceeding the 95% confidence level above a red noise background spectrum. (c) global wavelet spectrum indicating a peak variance at ~90 years above the white noise background indicated by the dashed line. Although higher frequency variability is identified near 500 y BP, its presence is not significant enough to be detectable on the global wavelet spectrum.
Figure 17 - Wavelet spectral analysis of CR1 $\delta^{18}$O. (a) Normalized, detrended CR1 $\delta^{18}$O time series plotted with the x-axis in years BP (b) CR1 wavelet power spectrum with warmer colors indicating increasing variance. Black lines encircle variance exceeding the 95% confidence level. (c) Global wavelet spectrum indicating a peak at a period of ~90 years above the white noise background spectrum.
CHAPTER 7
DISCUSSION

7.1 Introduction

Analysis of CR1 stable isotope values allows for the reconstruction of a regional precipitation record and through the teleconnections of the climate of Southeast Brazil to other parts of the world has implications for continental and global scale change. This information can be used to address a variety of questions related to local precipitation variability, forcing factors and possible interhemispheric relationships. In addition to larger scale implications of the CR1 record, it is also important to address the validity of apparent relationships between features of the record associated with the Little Ice Age as well as coherence between CR1 and other paleoclimate proxies of similar extent and resolution.

7.2 CR1 as a Indicator of Precipitation Seasonality and Amount

One critical question to address for speleothem records of any type is what climatologically parameter (if any) is archived in the sample. For speleothems, $\delta^{13}$C and $\delta^{18}$O are often thought to be direct recorders of drip water stable isotope values. This assumption however, must be validated. It is vital to establish that CR1 is faithfully recording drip water (and thereby precipitation) $\delta^{18}$O without the influence of kinetic or evaporative effects. Only then is it reasonable to try and identify climate parameters likely to influence the $\delta^{13}$C and $\delta^{18}$O composition of speleothem calcite.
7.3 CR1 as a Reliable Recorder of Cave Drip Water $\delta^{18}\text{O}$ and Precipitation $\delta^{18}\text{O}$

Many variables are involved in determining whether or not speleothems are accurate recorders of precipitation $\delta^{18}\text{O}$. Foremost are in-cave kinetic fractionation and evaporative effects. It is important to address the possibility that these processes may have influenced CR1 $\delta^{18}\text{O}$ and/or $\delta^{13}\text{C}$.

One of the simplest ways to avoid problems associated with evaporation is to select samples that are far away from cave entrances. Such passages are typically not subject to dramatic changes in temperature or humidity on millennial time scales. Although CR1 was collected relatively near the entrance of Cristal Cave (~100 meters), the cave entrance is small and restricts airflow between the cave and surface. The outside relative humidity is also ~90%, helping to ensure that the cave atmosphere remains near 100% RH.

It is also possible to detect kinetic or evaporative fractionation effects after the sample is collected with the “Hendy Test” based on the degree of correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. CR1 does not show significant correlation between stable isotope values in either form of the “Hendy Test” either along growth layers or along the growth axis (Figures 11 and 12). Both of these results point to a significant lack of evaporation or kinetic fractionation effects during calcite precipitation, suggesting that CR1 is a faithful recorder of dripwater oxygen isotope values.

Because CR1 grew during the late Holocene we can eliminate the possibility that stable oxygen isotope values are responding to ice volume change. In addition, it is unlikely that the carbon isotope values are influenced by a change in vegetation type (from C3 to C4 photosynthetic pathway). Though age does not directly play a role in
affecting speleothem $\delta^{13}C$ values, large scale vegetation changes often influence $\delta^{13}C$.

Typically, climate driven changes in vegetation take place over millennia, not 4,100 years as is the case with CR1. It is possible that anthropogenically driven changes in vegetation (for example clearing of rainforest for crops such as corn) may influence speleothem $\delta^{13}C$ values but the native deciduous rainforests have stayed intact over the late Holocene (Behling, 2002) Additionally, CR1 $\delta^{13}C$ do not display the range of variability typically associated with C3 versus C4 vegetation type. In short we conclude that CR1 is primarily recording variability in the stable isotopic composition of precipitation which in turn, is governed by moisture source location and indirectly, the amount effect.

7.4 Modern Controls on Precipitation $\delta^{18}O$ in Southeastern Brazil

To form accurate hypotheses regarding past precipitation variability in southeastern Brazil and likely links to precipitation (and therefore speleothem) $\delta^{18}O$, it is best to fully examine modern controls on the stable isotopic composition of precipitation in the region. Processes such as the annual migration of the ITCZ and subsequent development of the SAMS play a large role in determining precipitation $\delta^{18}O$. In Southeastern Brazil precipitation falling during the austral summer or winter is sourced, respectively, from either the Amazon Basin or nearby subtropical Atlantic. These two sources are isotopically distinct and the relative percentages of each control the annual mean isotopic signature of precipitation. Assuming that circulation patterns over South America during the late Holocene have remained more or less similar to modern day suggests that speleothem $\delta^{18}O$ values that are indicative of moisture source location and/or seasonality of precipitation (Cruz et al., 2005a, 2005b). This relationship is
assumed to have operated during the past 4.1 kyr much the same way as today. Thus, it becomes important to investigate what parameters affect the relative concentrations of winter versus summer precipitation, and also those that may affect the isotopic composition of winter or summer precipitation. For example, what role might ENSO and other SSTs anomalies play in regulating precipitation stable isotope values.

The fact that precipitation moisture source (summer = Amazon Basin vs. winter = Southeastern Atlantic) is the main driver of precipitation δ18O in southeastern Brazil is often used to explain modern precipitation δ18O values recorded in Porto Alegre (Figure 18) approximately 650 km south of Cristal Cave. Figure 18 indicates that precipitation δ18O and precipitation amount are not related. There are two peaks of precipitation amount observed at Porto Alegre, one occurring during austral winter (approximately September) the other occurring in austral summer (approximately February). The fact that two peaks of similar magnitude have distinct δ18O values shows that an amount effect does not govern the isotopic composition of modern precipitation in southeastern Brazil.

Instrumental records indicate that an amount effect does not govern precipitation δ18O. However, when CR1 δ18O is plotted against instrumental precipitation records a “localized” amount effect may be detectable (Figure 19). A peak in precipitation amount recorded during the early 1980’s is followed by a corresponding decrease of CR1 δ18O, a relationship that would be the expected result of an amount effect. It is possible that during austral spring and fall (specifically October and April) atmospheric circulation mechanisms governing precipitation δ18O (primarily the SACZ) have not yet fully developed. Vuille and Werner (2005) state that the SACZ is best developed during the
summer (DJF). During times when the SACZ is fully active the vertical convection and
preferential rainout of heavy isotopes during moisture transport are most active, thereby
yielding a strong precipitation moisture source location signal during DJF. During the
austral winter these mechanisms are not active and precipitation is more locally sourced.
Thus, during austral spring and fall a localized amount effect may be active.
Figure 18 - Yearly precipitation amount and mean $\delta^{18}$O composition for IAEA GNIP monthly station at Porto Alegre (Cruz et al, 2005).
7.5 CR1 Stable Isotope Values and Instrumental Records

Direct comparison between CR1 stable isotope values and instrumental precipitation records is possible due to the high temporal resolution of the stable isotope record, the high quality of the age model and the fact that CR1 was actively growing at the time of collection. An apparent relationship is noted in Figure 15 whereby CR1 $\delta^{18}$O and $\delta^{13}$C displays some features of both precipitation records. It should be noted that in Figures 15 and 16 vertical axes are oriented in a similar fashion such that increases in precipitation coincide with decreased $\delta^{18}$O.

![Cross correlation plot of Eldorado station precipitation values and CR1 $\delta^{18}$O. Maximum correlation of .5 occurs at a time lag of 5.1 years.](image)

CR1 $\delta^{18}$O broadly follows precipitation amount even though it has been demonstrated that the amount effect does not dominate in southeastern Brazil (Cruz et al., 2005; Vuille and Werner, 2005). To better quantify any potential relationship between
precipitation amount and CR1 δ¹⁸O values, a non-normalized cross correlation using FFT without a mean was applied (Figure 19). At a time lag of zero the correlation coefficient is only $r^2 = -0.038$ but at 5.1 years $r^2 = 0.500$. Given the dating uncertainties in the most recent 126 years of CR1 ($\pm 9 \text{ y}$), it is reasonable to shift δ¹⁸O values 5.1 years to obtain a relevant correlation. The correlation between CR1 and instrumental precipitation records indicates that a localized amount effect may play a role in modulating precipitation δ¹⁸O even in a geographic area that is known to respond primarily to precipitation moisture source location signals (Cruz et al., 2005).

**7.6 ENSO Influence on Precipitation in Southeastern Brazil**

We also compared instrumental precipitation records from southeastern Brazil and the Multivariate ENSO Index (MEI), a measure that is used to quantify ENSO activity through a variety of parameters (Wolter and Timlin 1993, 1998). The MEI address several factors in order to quantify ENSO state including sea level pressure, zonal and meridional surface wind, sea surface temperature, surface air temperature and total cloudiness fraction of the sky (Wolter and Timlin 1993, 1998). Multivariate ENSO Index values are available throughout each year but for this investigation MEI values for December/January are used due to the fact that this is when the ITCZ is in its southernmost position and the locus of convection is centered over the continent during the austral summer. Positive values correspond to warm phase ENSO (El Niño) while negative values indicate cool phase ENSO (La Niña) events.

Figure 20 shows apparent relationships between precipitation amounts at both weather stations and the MEI. Cross correlation analysis reveals that $r^2 = 0.28$ at a time lag of 3.1 years between MEI and Iporanga station data and $r^2 = 0.31$ at a time lag of 1 year
between MEI and Eldorado station data. Overall, it is apparent that during periods of positive MEI (warm ENSO) there is relatively greater rainfall in southeastern Brazil. Unfortunately, this relationship is not well represented in CR1 $\delta^{18}$O for the entire instrumental period. Although trends and segments of the data exist that appear to offer correlation within dating error ($r^2 = .18$ at a time lag of 14 years), no strong and persistent relationships are noted. Generally depleted $\delta^{18}$O during the late 1980’s may be related to more positive MEI values and near zero averaged MEI values during the 1950’s to 1970’s are reflected by relatively unchanging CR1 $\delta^{18}$O (Figure 15).

Figure 20 – Instrumental precipitation records plotted with the Multivariate ENSO Index (MEI) (Wolter and Timlin 1998).
7.7 Interpreting Trends and Notable Features of the CR1 Record

The first order trend of $\delta^{18}O$ in CR1 is a general decrease from 4 kyr BP to modern day. Although the trend of increasingly negative values persists throughout the record, some of the most positive values are observed within the past several hundred years. The general trend of increasingly negative $\delta^{18}O$ likely results from an increase in summer solar radiation, an increase in the intensity of the SASM and southward migration of mean ITCZ position. As a result, the site of CR1 experienced proportionally more precipitation more summertime rainfall and/or increased precipitation volume from 4 kyr BP to today (Cruz et al., 2005) This interpretation is in agreement with work by Haug et al. (2001) whereby Cariaco Basin metal concentrations were used to identify an increasingly southern position of the ITCZ during the late Holocene. Work by Cruz et al. (2005) indicates that solar forcing related to the Earth’s precessional cycle is the primary driving mechanism of Holocene moisture availability during the Holocene and has shown this relationship to hold true on timescales over ~100 kyr. It is assumed that if Southern Hemisphere summer insolation values dominate the millennial scale trend of other southeastern Brazil speleothems that this relationship will also hold true for CR1. This relationship between can be noted in Figure 21 whereby steadily increasing amounts of summer insolation correlate to generally decreasing CR1 $\delta^{18}O$. 

The overall trend of CR1 $\delta^{18}$O indicates increasingly negative values leading towards modern day yet the occurrence of numerous excursions should not be overlooked. Perhaps most notable is the $\sim -2\%$ excursion during the LIA interval. According to our interpretation of CR1 $\delta^{18}$O, this period is marked by the highest precipitation amounts as well as proportionally high amounts of summer time rainfall in the record. The LIA signal recorded by CR1 is also preserved in several other proxy records from South America, as will be discussed later. It should be noted that the periods immediately before and after the LIA interval are the driest (with proportionally more winter rainfall) than any other period covered by CR1.

The LIA interval recorded by CR1 $\delta^{18}$O is notable not only for its significant negative excursion, but because it marks a period of extremely high variability in a relatively short interval of time. Wavelet analysis (Figure 17) confirms that the period
from ~500 to 100 y BP contains a significant (above the 95% confidence interval) cyclicity of ~ 90 years. This cyclicity is also noted in the record near ~3 kyr BP but is not as pronounced. It is possible that cyclicity observed within the CR1 δ¹⁸O record is due to the Wolf-Gleissburg cycle, known to have a periodicity of 80 years (Yousef, 2000). Though not all solar cycles have an appreciable influence on climate it is difficult to explain a cycle with a ~ 90 year periodicity without invoking a solar mechanism.

7.8 CR1 and Other Proxies

Comparison between multiple proxies often allows for identification of trends or features that may not otherwise be detectable or deemed significant. Relationships between proxies (whether or not they are geographically distal) can often yield clues concerning larger scale change that may not appear significant or even be detectable within a single proxy. Direct comparison between CR1 and other proxies was limited to paleo-archives that record late Holocene change at a comparable resolution.

7.8.1 Southeastern Brazil Speleothems

CR1 offers a nearly annually resolved record of climate change over southeastern Brazil for the late Holocene. Currently there are no published records of similar length and resolution, though there are several published reports of speleothems from the region (Cruz et al., 2005a 2005b, Wang et al., 2006). These records extend to more than 100 kyr but generally with only sub-centennial resolution. Figure 22 shows CR1 δ¹⁸O values plotted against BTV4a (Wang et al., 2006) and Bt2 (Cruz et al., 2005a 2005b) δ¹⁸O collected from Botuverá Cave, 300 km away from Cristal Cave. There is a significant difference between stable isotopic values from the two geographically close stalagmites. On average, BTV4a values are nearly 1.5‰ greater than CR1 and Bt2 δ¹⁸O is typically
2‰ greater. This difference probably reflects the location of Cristal Cave, which lies closer to the center of the SACZ.

Due to the fact that samples from Botuverá are of much courser resolution than CR1, it is not appropriate to directly compare stable isotope values for specific periods of interest. Instead, it may be more meaningful to look at trends. Bt2 does not display any detectable trend over the last 4.1 kyr, however Btv4a shows an average decrease of 1‰ over the same time interval. This trend is similar to but somewhat smaller in magnitude than the trend in CR1.

Figure 22 - CR1 $\delta^{18}$O plotted with Bt2 and BTV4a $\delta^{18}$O, both from nearby (~300 km) Botuverá Cave. Bt2 shows no detectable trend yet mean values for Btv4a decrease ~ 1‰ towards modern day.

7.8.2 Cariaco Basin Sediments

The laminated sediments of the anoxic Cariaco basin provide one of the most well studied proxy records for climate in northern South America (Haug et al., 2001, 2003). Variability recorded at Cariaco is relevant to changes in speleothem calcite $\delta^{18}$O observed in southeastern Brazil because annual migration of the ITCZ and the associated
convection is largely responsible for precipitation variability observed at both locations. In the most simple case it is expected that when the mean position of the ITCZ is furthest north, precipitation in southeastern Brazil will be reduced. Relationships between Cariaco Basin sediments and CR1 $\delta^{18}$O are important because they may yield insight concerning global scale climate dynamics.

Figure 23 - CR1 $\delta^{18}$O plotted with Cariaco Basin sedimentary titanium concentrations. Apparent anticorrelations are noted whereby low concentrations of Cariaco Basin titanium (indicative of dry conditions) are associated with relatively low speleothem $\delta^{18}$O (indicative of wet conditions). Also note the axis for Cariaco Basin titanium concentration whereby drier conditions are indicated by smaller values. Cariaco titanium data after Haug et al. (2001).

Stable isotope values and Cariaco Basin titanium concentrations show remarkable anticorrelation over the past 4.1 kyr (Figure 23). Overall trends for the entirety of the records show a gradual decrease in Cariaco Basin titanium concentrations along with a gradual decrease of CR1 $\delta^{18}$O. Superimposed on these trends are several excursions that are also anticorrelated including visibly detectable periods from ~650 y BP to modern day and ~1610 to 1210 y BP. The entirety of the two records have a cross correlation.
coefficient of $r^2 = .348$ at a time lag of zero years, indicating a statistically significant relationship between the two. Although maximum anticorrelation is present at a time lag of approximately zero there are visually detectable lead/lag relationships between the two records. Most notably, CR1 $\delta^{18}O$ leads Cariaco Basin titanium records including periods near 1270 y BP and 2345 y BP. In part, the apparent lead/lag relationship at these timescales may be due to errors in respective age models. The radiocarbon dating of Cariaco Basin sediments is not as accurate as U/Th dating of CR1 and cumulative dating errors result in an offset of ages for various subsamples. Nevertheless, Cariaco Basin sediments provide a vital record of climate change in South America that can be related to global scale processes and to change archived in CR1. This is possible in large part due to the fact that Cariaco Basin sediments primarily record the mean position of the ITCZ (Haug et al., 2001), a feature that has far reaching influence.

One of the most striking features of the Cariaco titanium record and CR1 $\delta^{18}O$ is that both display notable trends leading towards modern day. A strong anticorrelation is noted whereby steadily decreasing CR1 $\delta^{18}O$ is associated with decreasing Cariaco titanium values. This is the relationship one would expect if mean position of the ITCZ is the dominant control on precipitation variability observed at both locations. Work by Haug et al. (2001) first identified the general trend in Cariaco metal concentrations and attributed it to a southward migration of the ITCZ. This migration is largely attributed to changes in the seasonality of insolation linked to the ~23 kyr precessional component of Milankovich forcing (Haug et al., 2001). Similarly Cruz et al. (2005) determined that summer solar radiation plays a dominant role in determining the $\delta^{18}O$ of precipitation.
(and therefore speleothem calcite) in southeastern Brazil and detected an apparent cyclicity of ~20 ka in stalagmite Bt2.

### 7.8.3 CR1 and the Wanxiang Speleothem Record

Further afield, Wanxiang Cave (33º 19’N, 105º 00’E) provides a high resolution, well dated speleothem record of Asian Monsoon (AM) intensity (Zhang et al., 2008) with which to compare CR1. Wanxiang Cave is situated favorably such that changes in precipitation $\delta^{18}O$ are indicative of Asian Monsoon (AM) intensity via an amount effect acting on precipitation. Thus, more negative $\delta^{18}O$ values of the Wanxiang speleothem (sample WX42B) are indicative of increased AM intensity. The Wanxiang $\delta^{18}O$ record is useful for comparison with CR1 because both speleothems offer records at similar resolution. Other speleothems from China (Wang et al., 2001) present similar data but at a much coarser resolution. Research on Chinese speleothems in conjunction with those from South America (Wang et al., 2005) has revealed that large portions of speleothem $\delta^{18}O$ interpreted as AM variability anticorrelate with low latitude Southern Hemisphere records. Minima in $\delta^{18}O$ of Chinese speleothems are correlated with maxima in $\delta^{18}O$ of speleothems from southeastern Brazil (Wang et al., 2006). Wang et al. (2006) interpret this interhemispheric anticorrelation largely as the result of the mean north/south position of the ITCZ as well as Hadley circulation asymmetry, an interpretation similar to that of Zhang et al. (2008). Regardless of the specific locality, monsoon intensity in the Northern and Southern Hemisphere are inversely related due to common control by the mean location of the ITCZ and/or asymmetry in Hadley cell circulation.

Perhaps most importantly for this investigation, comparison between CR1 and Wanxiang $\delta^{18}O$ (Figure 24) shows that previous hypotheses posed relating to the mean
position of the ITCZ and its influence on AM and SAMS intensity hold true over time scales much shorter than the millennial and orbital ones already invoked (Zhang et al., 2008; Wang et al., 2007, 2006). In regards to teleconnections, Wang et al. (2006) have determined that interhemispheric teleconnections exist and are detectable in speleothems from southeastern Brazil as well as China. Due to the relationships observed between northern and southern hemispheres it is likely that the annual migration of the ITCZ and its mean northern and southern position is responsible for concordant changes in calcite (and therefore speleothem) $\delta^{18}$O observed at both locations.

![Figure 24 - CR1 $\delta^{18}$O plotted with Wanxiang $\delta^{18}$O](image)

**7.8.4 CR1 with Quelccaya Ice Cores**

Tropical ice cores offer the opportunity to compare change recorded in CR1 against geographically proximal, equally high resolution archives. The Quelccaya ice core offers one of the most complete and high resolution records available (13°56’S, 70°50’W). Though many parameters of a single ice core often yield relevant data, ice
core conductivity and ice $\delta^{18}$O serve as one of the most important indicators of change observed in CR1. Perhaps one of the most readily apparent features of the CR1 stable isotope record is an approximately -2‰ excursion during the LIA. This excursion may be caused by several processes and by examining the CR1 stable isotope record in relation to Quelccaya data it may be possible to further delineate the role various processes play.

Pioneering work on Quelccaya ice cores by Thompson et al. (1986) relates observed increases in microparticle concentration and conductivity to increases in atmospheric loading of particles, not simply decreased snow accumulation rates. These factors may be related to the average position and convective intensity associated with the mean position of the ITCZ during the austral summer. As Thompson et al. (1986) points out, increased particulate concentrations are associated with increased wind velocity as well as increased aridity across the Altiplano. It is possible that an intensified and/or increasingly southern mean position of the ITCZ will result in increased dust levels via greater wind velocity across the Altiplano. The increased particulate concentrations noted during the LIA correlate well with CR1 $\delta^{18}$O values which in turn indicate increased rainfall amount and/or increased summertime precipitation during this period (Figure 25). Though it is not necessarily quantifiable, it is appropriate to state that some relationship exists between aridity and surface wind velocity on the Altiplano and speleothem calcite $\delta^{18}$O in southeastern Brazil.

It should also be noted that Quelccaya $\delta^{18}$O and CR1 $\delta^{18}$O are both broadly correlated, including the LIA interval (Figure 26). During ~ 300 yr BP, CR1 $\delta^{18}$O indicates proportionally more summer precipitation as well as increased precipitation
amount. This interval corresponds to Quelccaya $\delta^{18}O$ values that indicate relatively cooler conditions regionally along with cooler Northern Hemisphere conditions according to relationships proposed by Thompson et al. (1986). This relationship helps to further establish that the Little Ice Age was global in scope and is detectable in the Southern Hemisphere as synchronous excursions in CR1 and Quelccaya $\delta^{18}O$.

Figure 25 - CR1 $\delta^{18}O$ plotted with Quelccaya conductivity values (Thompson, 1992). Note the general increase in conductivity during ~440 – 150 BP, coinciding with a decrease in CR1 $\delta^{18}O$ and the LIA period.
7.8.5 CR1 with Lake Pallcacocha Sediment Red Color Intensity

Situated in the southern Ecuadorian Andes, Lake Pallcacocha provides a record of Late Holocene climate change via laminated sediments. Multiple occurrences of light colored inorganic laminae are hypothesized to correlate with periods of locally high rainfall that are driven by ENSO variability (Figure 27) (Moy et al., 2002). This proxy is useful in regards to CR1 stable isotope values because it offers a record that is of similar length and resolution as CR1 and is a likely indicator of ENSO occurrence. However it is important to note that red color intensity is not a direct proxy for warm ENSO occurrence. Instead, Moy et al. (2002) constructed an “event model” in order to identify the number of warm ENSO events occurring over each 100 year period of the record, shown plotted against CR1 $\delta^{18}$O values in Figure 28. The Lake Pallcacocha red color
intensity record shows little overt correlation with CR1 $\delta^{18}$O, possibly confirming hypotheses posed by Moy et al. (2002) stating that red color intensity is not directly attributed to ENSO events.

Figure 27 - CR1 $\delta^{18}$O plotted with Lake Pallcacocha sediment red color intensity. Increasing Red Color Intensity values indicate relatively greater amounts of local precipitation.

Figure 28 - CR1 $\delta^{18}$O values plotted against ENSO occurrence (Moy et al., 2002). Dashed line at ~5 Events per 100 years indicates the minimum number of events per 100 years needed to produce ENSO variance in Lake Pallcacocha red color intensity.
Though CR1 δ\textsuperscript{18}O and Lake Pallcacocha red color intensity appear to show little correlation, the most recent 500 years are somewhat anticorrelated ($r^2 = -0.31$ at time lag of -37 years). Again, the apparent time lag is well within the total dating errors of the two archives. Although the timing is not identical, there are clearly periods when CR1 indicates simultaneously increasing precipitation amount/increasing summer precipitation and Lake Pallcacocha indicates relatively little clastic runoff as would be expected from the modern relationship between ENSO and rainfall in southeastern Brazil. We also investigated the relationship between CR1 δ\textsuperscript{18}O and ENSO occurrence as determined by Moy et al. (2002) and shown in Figure 28. Individual 100 year periods of warm ENSO events do not appear to correlate well with the timing or amplitude of changes in the CR1 δ\textsuperscript{18}O record. Garreaud et al. (In Press) point out that the amplitude of ENSO related anomalies is not always consistent because other mechanisms may surpass ENSO influence or changes in ENSO behavior may alter teleconnections. However, there may be some relationship between ENSO and CR1 as periods of high variability in both records coincide during the most recent 1.2 kyr BP. Perhaps it is this extended period of ENSO events that leads to increased variability in the CR1 record along with increased amount/summertime distribution of precipitation in southeastern Brazil. In fact, Garreaud et al. (In Press) note that warm ENSO events typically coincide with increased precipitation over southeastern Brazil.

7.9 Trends and Variability of CR1 δ\textsuperscript{13}C

The basis of far reaching hypotheses on a single variable (in this case speleothem δ\textsuperscript{18}O) may not be ideal but is necessary in some cases due to lack of supporting data. Fortunately in the case of CR1, concordant δ\textsuperscript{13}C values are available with which to
further support or refute hypotheses. This is possible because variability of speleothem calcite $\delta^{13}C$ is typically attributed to changes in vegetation type as well as bacterial activity within soil overlaying a cave (Cruz et al., 2006). Geochemical modeling studies indicate that speleothem carbonate values between -12‰ and -6 ‰ are associated with dominantly C3 type vegetation in the catchment area and relatively high values (-6 to +2 ‰) are thought to reflect C4 type vegetation (Dreybrodt, 1980). Though these relationships are not always present (Baker et al., 1996), there are some instances where $\delta^{13}C$ has been reliably tied to vegetation type (Cruz et al., 2006). Typically when vegetation changes are invoked to explain fluctuations in speleothem $\delta^{13}C$, time scales on the order of tens of thousands of years are required to adequately allow for significant vegetation change. However in certain cases, anthropogenic modification of the landscape for agriculture may play a role (Blyth et al., 2007). In the case of CR1, the time scale is too short to adequately allow for climatologically driven moisture availability and temperature driven changes in vegetation to be the dominant control of $\delta^{13}C$. Instead it is likely that fluctuations in moisture availability influence rates of organic production and decay along with the degree of calcite saturation of infiltrating water. Increased plant respiration and microbially mediated decomposition of organic matter within soil results in more negative soil $\delta^{13}C$ (Amundson et al., 1998) These changes are likely to fluctuate with a relatively high frequency and the rate of organic production and decay may be localized, relatively short term processes. Whatever the mechanism, it is likely that there are multiple drivers of variability in the CR1 $\delta^{13}C$ record and that individual mechanisms are not easily delineated (Baker et al., 1996), however long term trends and significant excursions likely offer insight concerning moisture availability.
Perhaps if decadal and interannual changes in moisture availability are responsible for fluctuations in $\delta^{13}C$ then the instrumental precipitation record from both Iporanga and Eldorado may offer insight on possible forcing mechanisms. Figure 9 shows a trend in CR1 $\delta^{13}C$ that is very similar to $\delta^{18}O$. Both of these records broadly follow instrumental precipitation at both weather stations. This relationship is to be expected in a setting where increased precipitation and thus increased soil moisture availability lead to increased organic decay and microbial activity in the soil zone. This increase in microbial activity would likely lead to isotopic depletion of stable carbon isotopes. Barring any influence of kinetic or evaporative fractionation effects between soil and speleothem, it is possible for depleted $\delta^{13}C$ values to be recorded in speleothem calcite. If this relationship holds true it may be possible to extrapolate precipitation amounts prior to instrumental records based on a combination of $\delta^{13}C$ and $\delta^{18}O$ values and trends. At the very least, it is likely appropriate to extrapolate precipitation amounts in a relative sense.

One of the greatest assumptions concerning the extrapolation of $\delta^{13}C$ into precipitation amount on the basis of soil moisture availability is that the relationship between $\delta^{13}C$ and precipitation amount is linear. In all likelihood there is an upper and lower limit on the influence of soil moisture on microbial activity and organic decay in the soil zone. It is likely that either too much or too little soil moisture will adversely affect $\delta^{13}C$ values resulting from microbial activity. With these potential problems in mind, it is appropriate to say that significant portions of the CR1 record possesses $\delta^{13}C$ values which are indicative of conditions wetter than modern day. Most notable among
these excursions is the period between ~ 285 and 545 yr BP (LIA). Extrapolating the modern relationship between δ¹³C and precipitation amount makes it is possible to state that during this interval, yearly precipitation amounts were at least 1,700 mm/yr, approximately equivalent to the peak precipitation amount recorded at Iporanga in 1982.

Interpretation of δ¹⁸O and δ¹³C in order to yield absolute precipitation amounts over the duration of the CR1 record may not yield totally accurate values however it is possible to interpret both records simultaneously in order to yield more credible results. In the case of CR1, it may be most appropriate to use δ¹³C to substantiate interpretations based primarily on δ¹⁸O. Assuming that depleted δ¹³C is indicative of increased moisture availability and therefore increased microbial activity in the soil, then it is appropriate to state that increasingly negative δ¹³C leading towards modern day support the notion that δ¹⁸O indicates greater precipitation and/or an increasing proportion of summer precipitation. The relationship between δ¹⁸O and δ¹³C holds true over much of the CR1 record with notable periods such as the LIA represented as a general decrease in values, thereby supporting the hypothesis that this time period was relatively wet. Instrumental records of precipitation amounts (Figure 19) indicate that increasingly negative δ¹⁸O and δ¹³C generally corresponds to increasing precipitation amounts, lending further credibility to hypotheses posed regarding general precipitation trends and δ¹³C prior to the instrumental record.
CHAPTER 8
CONCLUSIONS

Precipitation variability over the last 4.1 kyr BP in southeastern Brazil has been governed by mean southern position of the ITCZ and associated convection over the Amazon Basin. The intensity of convection is largely responsible for determining the amount and seasonality of precipitation falling in the region, however the southward migration of the ITCZ and associated onset of the SAMS is likely modulated by ENSO on decadal timescales. On millennial and longer time scales, precipitation is controlled by insolation and increasingly greater amounts of summer insolation towards modern day are reflected by an increasing proportion of summer precipitation. It is likely that CR1 is able to quickly respond to forcing mechanisms related to changes in insolation due to the fact that much of the summer precipitation regime in southeastern Brazil is governed by convection associated with the SAMS.

The trend of $\delta^{18}O$ that indicates increased moisture availability is in agreement with other proxies from southeastern Brazil. Although the overall trend is dictated by millennial scale changes, shorter excursions of $\delta^{18}O$ and $\delta^{13}C$ indicate that CR1 is capable of recording events lasting centuries (such as the LIA) as well as much shorter “point-like” events including localized increases in precipitation amount lasting on the order of several years.

Instrumental records of precipitation variability can be roughly calibrated to variability observed in CR1 $\delta^{18}O$ because of the high precision of the age model associated with it. This direct comparison indicates that the range of precipitation amount
observed during the last ~60 years is relatively small compared to the extent of past
variability. During the Little Ice Age, precipitation was likely greater than peak
precipitation observed during the early 1980’s (average 1700 mm at Eldorado and
Iporanga stations). Disregarding the century scale excursion associated with the LIA,
much of the CR1 stable isotope record indicates gradually greater and/or an increased
summer precipitation proportion leading towards modern day.
### APPENDIX

### ADDITIONAL DATA

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<td>CR1-1</td>
<td>308.67</td>
<td>y = (x+68.725)/.2848</td>
</tr>
<tr>
<td>CR1-31.8 mm</td>
<td>446.45</td>
<td>y = (x+9.124)/.0917</td>
</tr>
<tr>
<td>CR1-44.6 mm</td>
<td>592.25</td>
<td>y = (x+7.395)/.0878</td>
</tr>
<tr>
<td>CR1-72 mm</td>
<td>780.73</td>
<td>y = (x+3.8135)/.0689</td>
</tr>
<tr>
<td>CR1-84 mm</td>
<td>992.91</td>
<td>y = (x+3.8135)/.0689</td>
</tr>
<tr>
<td>CR1-118 mm</td>
<td>1131.12</td>
<td>y = (x+13.748)/.0864</td>
</tr>
<tr>
<td>CR1-4</td>
<td>1681.24</td>
<td>y = (x-36.309)/.0486</td>
</tr>
<tr>
<td>CR1-5</td>
<td>1922.04</td>
<td>y = (x+4.4659)/.0728</td>
</tr>
<tr>
<td>CR1-6</td>
<td>2484.10</td>
<td>y = (x-19.786)/.0602</td>
</tr>
<tr>
<td>CR1-7</td>
<td>3230.30</td>
<td>y = (x+355)/.0683</td>
</tr>
<tr>
<td>CR1-8</td>
<td>3737.80</td>
<td>y = (x-19.113)/.0623</td>
</tr>
</tbody>
</table>

Table summarizing formulas used to linearly interpolate ages of CR1 between sub-sample locations
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Weight (grams)</th>
<th>$^{238}\text{U}$ (ppb)</th>
<th>$^{232}\text{Th}$ (ppt)</th>
<th>$d^{234}\text{U}$ (measured)</th>
<th>$[^{230}\text{Th}/^{232}\text{U}]_{\text{activity}}$</th>
<th>$[^{230}\text{Th}/^{232}\text{U}]_{\text{ppm}}$</th>
<th>Age uncorrected</th>
<th>Age corrected</th>
<th>$d^{234}\text{U}_{\text{total corrected}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR1-3.25 mm</td>
<td>0.1996</td>
<td>507.7 ± 1.5</td>
<td>134 ± 4</td>
<td>435.4 ± 4.6</td>
<td>0.00167 ± 0.00012</td>
<td>105 ± 8</td>
<td>127 ± 9</td>
<td>121.57 ± 9</td>
<td>435.5 ± 4.6</td>
</tr>
<tr>
<td>CR1-11 mm</td>
<td>0.2105</td>
<td>580.7 ± 2.3</td>
<td>118 ± 3</td>
<td>431.7 ± 5.6</td>
<td>0.00372 ± 0.00010</td>
<td>301 ± 12</td>
<td>284 ± 8</td>
<td>279.98 ± 8</td>
<td>432.1 ± 5.6</td>
</tr>
<tr>
<td>CR1-1</td>
<td>0.3570</td>
<td>2240.0 ± 5.6</td>
<td>238 ± 2</td>
<td>451.1 ± 3.6</td>
<td>0.00412 ± 0.00009</td>
<td>640 ± 15</td>
<td>311 ± 7</td>
<td>308.67 ± 7</td>
<td>451.5 ± 3.6</td>
</tr>
<tr>
<td>CR1-11.8 mm</td>
<td>0.2430</td>
<td>630.6 ± 2.7</td>
<td>160 ± 3</td>
<td>463.6 ± 6.9</td>
<td>0.00604 ± 0.00009</td>
<td>393 ± 9</td>
<td>451 ± 7</td>
<td>446.45 ± 7</td>
<td>464.1 ± 7.0</td>
</tr>
<tr>
<td>CR1-4.6 mm</td>
<td>0.2335</td>
<td>733.1 ± 5.2</td>
<td>59 ± 3</td>
<td>458.8 ± 5.4</td>
<td>0.00791 ± 0.00008</td>
<td>1618 ± 83</td>
<td>594 ± 6</td>
<td>592.25 ± 6</td>
<td>459.6 ± 5.4</td>
</tr>
<tr>
<td>CR1-2</td>
<td>0.5022</td>
<td>686.5 ± 2.1</td>
<td>77 ± 1</td>
<td>463.6 ± 2.5</td>
<td>0.01046 ± 0.00013</td>
<td>1536 ± 34</td>
<td>783 ± 10</td>
<td>780.73 ± 10</td>
<td>464.6 ± 2.5</td>
</tr>
<tr>
<td>CR1-72.0 mm</td>
<td>0.2472</td>
<td>616.8 ± 1.5</td>
<td>69 ± 3</td>
<td>446.1 ± 4.5</td>
<td>0.01312 ± 0.00010</td>
<td>1933 ± 80</td>
<td>995 ± 8</td>
<td>992.91 ± 8</td>
<td>447.3 ± 4.5</td>
</tr>
<tr>
<td>CR1-84 mm</td>
<td>0.2265</td>
<td>597 ± 1</td>
<td>258 ± 3</td>
<td>446.7 ± 4.3</td>
<td>0.01504 ± 0.00011</td>
<td>574.9 ± 8.3</td>
<td>1140.5 ± 9.2</td>
<td>1131.87 ± 10.1</td>
<td>448.1 ± 4.4</td>
</tr>
<tr>
<td>CR1-3</td>
<td>0.4365</td>
<td>883.3 ± 1.7</td>
<td>57 ± 2</td>
<td>456.5 ± 1.5</td>
<td>0.01643 ± 0.00014</td>
<td>4200 ± 123</td>
<td>1238 ± 11</td>
<td>1237.12 ± 11</td>
<td>458.1 ± 1.5</td>
</tr>
<tr>
<td>CR1-118 mm</td>
<td>0.2426</td>
<td>629 ± 2</td>
<td>157 ± 3</td>
<td>475.4 ± 4.6</td>
<td>0.02262 ± 0.00015</td>
<td>1497.8 ± 29.6</td>
<td>1686.2 ± 12.4</td>
<td>1681.24 ± 12.6</td>
<td>477.7 ± 4.6</td>
</tr>
<tr>
<td>CR1-4</td>
<td>0.4302</td>
<td>1012.9 ± 2.1</td>
<td>56 ± 2</td>
<td>478.1 ± 3.0</td>
<td>0.02583 ± 0.00022</td>
<td>7696 ± 232</td>
<td>1923 ± 17</td>
<td>1922.04 ± 17</td>
<td>480.7 ± 3.0</td>
</tr>
<tr>
<td>CR1-5</td>
<td>0.5307</td>
<td>714.2 ± 1.4</td>
<td>66 ± 1</td>
<td>467.0 ± 2.0</td>
<td>0.03036 ± 0.00025</td>
<td>5908 ± 126</td>
<td>2486 ± 19</td>
<td>2484.10 ± 19</td>
<td>470.3 ± 2.0</td>
</tr>
<tr>
<td>CR1-6</td>
<td>0.5295</td>
<td>1060.2 ± 3.1</td>
<td>805 ± 3</td>
<td>454.3 ± 2.3</td>
<td>0.04265 ± 0.00025</td>
<td>927 ± 5</td>
<td>3245 ± 20</td>
<td>3230.30 ± 21</td>
<td>458.5 ± 2.3</td>
</tr>
<tr>
<td>CR1-7</td>
<td>0.4302</td>
<td>1240.3 ± 3.4</td>
<td>144 ± 2</td>
<td>437.6 ± 2.1</td>
<td>0.04848 ± 0.00027</td>
<td>6905 ± 87</td>
<td>3740 ± 22</td>
<td>3737.80 ± 22</td>
<td>442.3 ± 2.1</td>
</tr>
<tr>
<td>CR1-8</td>
<td>0.4579</td>
<td>1678.4 ± 4.9</td>
<td>188 ± 2</td>
<td>382.1 ± 2.2</td>
<td>0.05105 ± 0.00030</td>
<td>7508 ± 76</td>
<td>4103 ± 26</td>
<td>4100.80 ± 26</td>
<td>386.5 ± 2.3</td>
</tr>
</tbody>
</table>
WORKS CITED


Cruz, F.W., Jr., 2007, Evidence of rainfall variations in southern Brazil from trace element ratios (Mg/Ca and Sr/Ca) in a late Pleistocene stalagmite: Geochimica Et Cosmochimica Acta, v. 71, p. 2250-2263.


Fairchild, I.J., 2000, Controls on trace element (Sr-Mg) compositions of carbonate cave waters; implications for speleothem climatic records: Chemical Geology, v. 166, p. 269-255.


Haug, G.H., et al., 2001, Cariaco Basin Trace Metal Data, IGBP PAGES/World Data Center for Paleoclimatology Data Contribution Series #2001-071. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA.


Thompson, L., 1992, Quelccaya Ice Core Database. IGBP PAGES/World Data Center for Paleoclimatology Data Contribution Series # 92-008. NOAA/NGDC Paleoclimatology Program, Boulder CO, USA.


